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Acetal copolymers: Syntheses and modification

Zheng, Yongchang, Ph.D.

City University of New York, 1992

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ACETAL COPOLYMERS:
SYNTHESES AND MODIFICATION

by

YONGCHANG ZHENG

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York.

1992

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

7/8/92
Date

Chair of Examining Committee

July 6, 1992
Date

Executive Officer

Prof. A. Woodward

Prof. M. Rafailovich
Supervisory Committee

THE CITY UNIVERSITY OF NEW YORK

Abstract

ACETAL COPOLYMERS:
SYNTHESES AND MODIFICATION

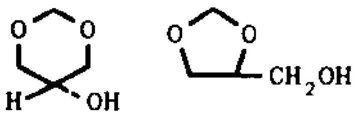
By

Yongchang Zheng

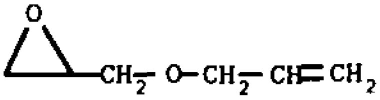
Adviser: Professor Nan-Loh Yang

Acetal polymers usually do not contain reactive functional groups other than hydroxyl end groups. The objective of this research is to synthesize acetal copolymers with functional groups which are reactive for further modification. For these purposes, cyclic ethers, such as:


Dioxane


Glycerol formal


1,3-Dioxep-5-ene


Allyl glycidol ether

and their derivatives are employed as comonomers.

In this study, the derivatives of dioxane, 5-ethyl-5-hydroxy-methyl-1,3-dioxane and its acrylate ester were synthesized and copolymerized with trioxane. Copolymerization of trioxane with 5-ethyl-5-hydroxymethyl-1, 3-dioxane is characterized by substantial chain transfer. The resulting copolymers are of low molecular weight ($3\text{-}6\times10^3$) but thermally stable. The pendant hydroxyl functional groups have been demonstrated to be reactive for further modification. Copolymerization of trioxane with acrylates of 5-ethyl-5-hydroxymethyl-1,3-dioxane gives a thermally stable copolymer with molecular weight up to $60x10^3$. The structures of these copolymers were studied in detail. The pendant acrylate functional groups are shown to be reactive with low molecular weight amines and polyamides with amine end groups.

Glycerol formal derivatives, such as glycerol formal acrylate, glycerol formal benzoate, and glycerol formal acetate, were also synthesized and copolymerized with trioxane. Copolymerization of trioxane with glycerol formal acrylate gives a copolymer with higher incorporation than the 1,3-dioxane system. This provides higher level of reactive sites for further reaction. Copolymers of trioxane with glycerol formal benzoate or glycerol formal acetate can be hydrolyzed in NaOH suspension to obtain high molecular weight acetal copolymer with hydroxyl groups.

Polyacetals with backbone and pendant epoxy functional groups were synthesized through the epoxidation of acetal copolymer with backbone or pendant double bond. The reactivity of backbone and pendant epoxy groups toward amines were determined, including primary and secondary amine. The pendant epoxy groups have been shown to be more reactive than the backbone epoxy groups and acrylate groups when react with amines, especially with secondary amine.

Acknowledgements

I would like to express my sincere gratitude to my mentor Professor Nan-Loh Yang for his support, guidance and encouragement as well as the preparation of this thesis.

Special thanks are extended to Professors A. Woodward and M. Rafailovich, members of my thesis committee, for their interest and advice as well as the generosity of their time.

During this thesis work, I was fortunate to interact in the lab with Chongli Zhang, Shizheng Zhu and Shiang Wang. Wang and Zhu did some preliminary work on the dioxane system. Mr. Zhang worked extensively on the dioxane and the glycerol formal systems. Some of our work overlaps.

Acknowlegement is gratefully made to the following sources of financial support: the Chemistry Department of College of Staten Island for teaching appointments from 1987-1992; graduate fellowship from Graduate School and University Center of City University of New York from 1986-1987 and Hoechst Celanese Corporation in summer of 1987.

I am indebted to J. Broussard, A. Auerbach, J. Paul, J. Starr and A. Forschirm of Hoechst Celanese for valuable interaction.

I am indebted to my parents and family for their faith and continuous support. Finally I would like to thank my wife, Jingyin Yang, for her support and understanding through all these years of my graduate studies at City University of New York.

Table of Contents

List of Tables

List of Figures

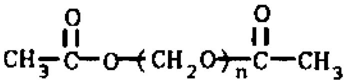
* All NMR spectra figures are with assignments.

1. Introduction

Acetal copolymers consist of oxymethylene structure with occasional insertion of comonomer units. The structure of the acetal homopolymer can be represented as:

$$HO\text{-}(CH_2O)_n\text{-}H\ .$$

The methylol end group, $-CH_2OH$, resulting from the polymerization is a hemiacetal and is unstable. The homopolymer may release formaldehyde molecules one by one from the chain ends[1] in a process called "unzipping". An end-capping reaction used for the prevention of the unzipping of polyacetals was developed by DuPont. The polymer is allowed to react with acetic anhydride, either in solution or heterogeneously in the presence of a catalyst such as sodium acetate[2] to give a thermally stable polymer:



$$CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}(CH_2O)_n\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_3$$

This end-capped homopolymer became a commercial product called **Delrin** in 1959. Shortly thereafter, an acetal polymer based on the copolymerization of trioxane with dioxolane or ethylene oxide[3] was developed by Celanese researchers . The unstable end groups from acetal copolymers can be removed through base hydrolysis of hemiacetal end block in the presence of alkaline media, either in solution[4] or heterogeneously[5]:

---

* References at the end of thesis listed by section.

$$HOCH_2CH_2{-}O{-}(CH_2O)_n(CH_2CH_2O)_m(CH_2O)_n{-}CH_2CH_2OH$$

The resulting end group, $-CH_2CH_2OH$, is no longer a hemiacetal and is stable. Thus, the comonomer units, $-CH_2CH_2O-$, are used as stable end groups and as stoppers against unzipping. This acetal copolymer was produced and designated **Celcon** in 1962. In general, acetal copolymers have better thermal stability. When the homopolymer molecular chain was occasionally broken down, it will be completely destroyed via chain unzipping. However, the copolymer will unzip only to the nearest comonomer unit.

Acetal copolymers are usually prepared from the copolymerization of trioxane and comonomer, such as ethylene oxide, in the presence of boron trifluoride etherate. Chain transfer with impurities can occur in the polymerization. It was found that water acts as a cocatalyst[6,7]. No polymer was obtained in this study if water was completely absent from the reaction system. Comonomer usually extends the induction period in copolymerization. In the case of copolymerization of trioxane with ethylene oxide, all ethylene oxide react before any trioxane is polymerized[8,9]. The comonomer reacts with formaldehyde generated from the opening of trioxane ring to form cyclic ethers, 1,3-dioxolane and 1,3,5-trioxepane until the ethylene oxide is consumed and then trioxane polymerization begins[7,10]. It was found that the distribution of comonomer units was random along the chain[11], due to the growing polymer chain undergoing a transacetalization reaction. In the transacetalization, the growing chain end attacks the acetal linkage of a portion of completed chain. As a result of this attack, one chain is terminated and a new growing chain is formed. This reaction may occur many times during the polymerization and is responsible to the narrow molecular weight distribution ($M_w/M_n=2$) observed in acetal polymers formed by cationic catalysis.

As mentioned above, the stabilization of acetal polymer is very important to their use as engineering plastics. Understanding of the modes of degradation needed to be overcome is necessary. These include the unzipping from the chain ends to yield monomeric formaldehyde, free radical and acidic attack on the acetal chain[12], and thermal scission which occurs above 270 °C[13]. Commercial polyacetals usually contain antioxidants to prevent degradation due to oxygen and peroxy radical degradation. Hindered phenols and aromatic amines are typical antioxidants to prevent oxidative chain degradation[14].

Acetal polymers usually do not contain any functional groups, except their hydroxyl end groups. Copolymer of trioxane with 1,3-dioxep-5-ene was shown to be a stable polyacetal with double bond in the backbone[15-18]. Comonomer 1,3-dioxep-5-ene acts as stable end groups and stopper against unzipping. Its double bond incorporated in copolymer can be sites for further modification. Copolymers of trioxane with glycerol formal[12], glycidyl acrylate[19], epichlorohydrin[20] have been explored.

The objective of this research is to synthesize acetal copolymers with functional groups which serve both as unzipping stoppers and reactive sites for further modification. This requires that comonomers possess reactive functional group which does not interfere with copolymerization with trioxane. The comonomer unit also acts as both stable end group after base hydrolysis of copolymer. For these purposes, a number of cyclic ethers and their derivatives are considered as comonomers.

The derivatives of dioxane, 5-ethyl-5-hydroxymethyl-1,3-dioxane and its acrylate esters were synthesized and copolymerized with trioxane. These copolymerizations lead to the copolymers with pendant hydroxyl and acrylate functionalities. The hydroxyl and acrylate groups are known to be reactive toward acylchlorides, isocyanates as well as amines respectively.

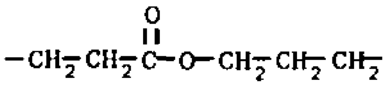
Glycerol formal is a cyclic acetal from formaldehyde and glycerin. Its derivatives, such as glycerol formal acrylate, glycerol formal benzoate, and glycerol formal acetate, were also synthesized and copolymerized with trioxane. Copolymer of trioxane and glycerol formal acrylate gives copolymer with acrylate functional groups. Copolymers of trioxane with glycerol formal benzoate and glycerol formal acetate lead to high molecular weight copolymers with hydroxyl groups through hydrolysis of the ester groups of the nascent copolymers.

In addition, acetal copolymers with pendant double bonds were synthesized using allyl glycidyl ether as comonomer. Polyacetals with backbone and pendant epoxy functional groups were synthesized through the epoxidation of acetal copolymer with backbone or pendant double bond. The reactivity of backbone and pendant epoxy groups were studied through reactions with primary and secondary amines. For reaction with amines, pendant epoxy functionality has been shown to be much more reactive than acrylate and backbone epoxy groups.

2. Copolymer of Trioxane with 1,3-Dioxane Derivatives

2.1. Introduction

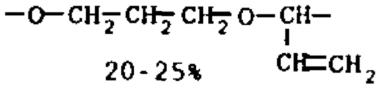
1,3-Dioxane (DOX) can be prepared by the acid-catalyzed reaction of propan-1,3-diol with paraformaldehyde. This compound is thermodynamically stable and has not been homopolymerized so far[1]. In the attempted polymerizations of DOX in bulk or in solution with perchloric acid as initiator, a mixture of cyclic dimers and trimers was obtained[2]. In contrast to 1,3-dioxane, 2-substituted 1,3-dioxanes, such as 2-vinyl- and 2-isopropenyl-1,3-dioxanes, are polymerizable by ring opening with cationic initiator[3]. These 2-substituted 1,3-dioxanes form light-yellow semi-solids or white powders in 10-30% yields in the presence of $SnCl_4$, $TiCl_4$ or $BF_3 \cdot Et_2O$ at 0 °C in heptane. The degrees of polymerization in these cases are relatively low (DP = 6-7, in the case of $TiCl_4$ initiation). With triethyl- oxonium tetrafluoroborate as the initiator and methylene chloride as the solvent, the DP ranges between 25 and 50[4]. The structures of the polymers of 2-vinyl-1,3-dioxane obtained in these cases consist of mainly three structural units. Chemical analysis and IR and NMR spectroscopic investigation established their presence in the indicated proportions[4]:



$-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-CH_2-$

5-10%

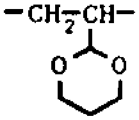
Isomerization



$-O-CH_2-CH_2-CH_2-O-\underset{CH=CH_2}{\underset{|}{CH}}-$

20-25%

Ring-opening polymerization

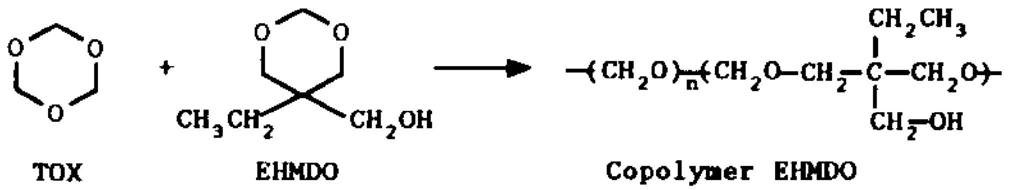


65-70%

Vinyl polymerization

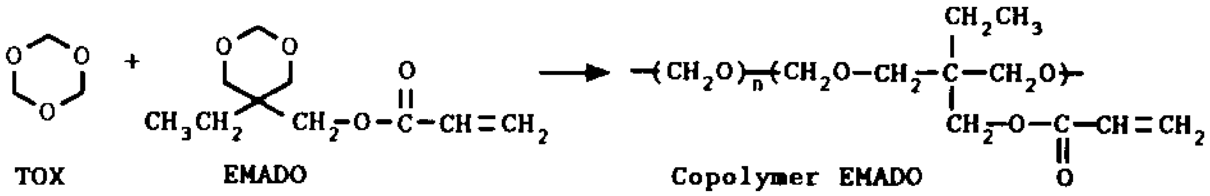
This suggests that vinyl polymerization is predominant under these conditions. Ring-opening polymerization with the formation of acrolein acetal units, as well as ring opening with hydride-transfer forming ester groups also occur to some extent. In the copolymerization of 2-vinyl-1,3-dioxane with styrene, or 1,3-dioxolane these three types of repeating units are also formed[5,6]. The polymerizations of 2-substituted 1,3-dioxanes and copolymerizations of these monomers with styrene at -80 °C using $BF_3 \cdot Et_2O$ as initiator have been described by Jedlinsky[5]. However, polymerizations of 5-substituted 1,3-dioxanes have not been reported.

In this study, 5-substituted 1,3-dioxane, such as 5-ethyl-5-hydroxymethyl-1,3-dioxane (EHMDO), was synthesized and copolymerized with trioxane using $BF_3 \cdot Et_2O$ as initiator to give acetal copolymers with pendant methylol, $-CH_2OH$, functional groups. The copolymerization is characterized by



substantial chain transfer. The resulting reactive low molecular weight acetal copolymers are potentially good candidates for the preparation of systems of structural composites requiring crystalline hard segments[7]

In addition, acetal copolymers carrying reactive pendant acrylate functionalities were prepared by the cationic ring opening copolymerization of trioxane with of 5-ethyl-5-methylacrylate-1,3-dioxane (EMADO).



The reactions of the polarized double bond separated by a four-bond spacer from the backbone of the resulting copolymers were investigated.

2.2. Experimental

2.2.1. Synthesis of 5-ethyl-5-hydroxymethyl-1,3-dioxane (EHMDO)

In a one-liter three neck flask were placed 405 grams (3.01 mole) of 2-ethyl-2-hydroxymethyl-1,3-propanediol, 90 grams (3.0 mole) of paraformaldehyde, 0.9 grams of *p*-toluene sulfonic acid monohydrate and 150 ml of toluene. The flask was equipped with a Dean-stark trap and a condenser. The reaction mixture was stirred at 120 - 170 °C for 3 hrs until the stoichiometric amount of water was collected in the trap. After removing toluene, the crude product was distilled under vacuum at 10 - 11 mm Hg. The portion (410 g) at 115 - 117 °C was collected. The product (EHMDO) was then dried by molecular sieve. Its water content was about 350 ppm.

2.2.2. Synthesis of 5-ethyl-5-methylacrylate-1,3-dioxane (EMADO)

Comonomer EMADO was prepared through the reaction of 5-ethyl-5-hydroxymethyl-1,3-dioxane (EHMDO) with acryloyl chloride. EHMDO (29.2 g, 0.2 mole), triethylamine (20.4 g, 0.22 mole), hydroquinone (10 mg) and toluene (50 ml) were placed in a 250 ml flask equipped with a dropping funnel and a drying tube. A toluene (20 ml) solution of acryloyl chloride (19.0 g, 0.21 mole) was added dropwise over a period of 15 min. into the solution kept cold in an ice water bath. The solid by-product ($Et_3N \cdot HCl$, 27 g) was removed by filtration and washed twice with toluene (2x15 ml). The collected filtrate was washed twice with water (2x20 ml) in a separatory funnel and separated. Purified comonomer EMADO was obtained through distillation of the filtrate under reduced pressure (b.p. 105-108 °C/5-6 mm Hg, yield 75 %).

2.2.3. Copolymerizations of trioxane with 5-ethyl-5-hydroxymethyl-1,3-dioxane and its acrylate

The copolymerization of trioxane with EHMDO and EMADO were carried out in bulk as well as in solution. The trioxane used was distilled at 104°C under the protection of dry nitrogen from sodium metal to remove water with benzophenone as indicator.

In the case of bulk copolymerization, the required amount (1 to 3 g) of comonomer was injected into a 25 x 150 mm test tube through a serum stopper capped on the test tube equipped with a magnetic stirrer, containing the desired amount of trioxane. The system was then placed in an oil bath. After the temperature reached 65 °C, 4 to 20 μl of $BF_3 \cdot Et_2O$ was injected. Within several seconds to several minutes depending on water content, the solution became immobilized by the growth of polymer throughout the flask. The copolymerization was allowed to proceed at 60 to 65 °C for 20 hrs.

In the case of solution copolymerization, the required amounts of trioxane and EHMDO were placed in a 100 ml round bottom flask containing 20 ml of cyclohexane. The solution was heated under stirring. When the temperature reached 65 °C, 20 μl of $BF_3 \cdot Et_2O$ was injected through a serum stopper every 2 minutes until copolymerization occurred to give a white precipitate. The total amount of initiator was about 60~100 μl for a feed of 10 g with a ratio of 9:1 (trioxane/EHMDO) by weight. Then the copolymerization was allowed to proceed at 65°C for 4 hrs.

The crude copolymers were ground into small chunks and washed with 1 % triethanolamine (TEA) methanol solution under stirring for 30~40 minutes. The copolymer was then washed with acetone 3 times and dried under vacuum at 50 °C.

2.2.4. Base hydrolysis of copolymers

The unstable end groups of copolymer and homopolymer of trioxane formed in the copolymerization were removed by base hydrolysis through a procedure described below. The crude polymer (10 g) in 100 ml of base hydrolysis solution, which contains N,N-dimethylformamide (DMF, 50 ml), benzyl alcohol (50 ml) and triethanolamine (TEA, 1 % of total volume), was placed in a 250 ml of round bottom flask fitted with an air-cooled, straight-through condenser and a magnetic stirrer. The contents were refluxed at 170 - 175 °C for 1 hour until evolution of formaldehyde was no longer visible. The polymer solution was cooled to room temperature and the solid polymer was filtered and washed with acetone three times. The polymer was then dried under vacuum at 40 °C.

2.2.5. Reactivity of copolymers with hydroxyl groups

An example for the reaction of copolymer functional hydroxyl groups is given as follows: A dry test tube (25x150 mm) was charged with 0.20 g of copolymer, 0.3 g of tripropylamine and 1.5 ml of toluene. Then 0.50 g of oleoyl chloride was added to the reaction mixture kept at the temperature range of 100-105 °C under stirring. The reaction was allowed to proceed for 1 hour. The product was collected by filtration, then washed with distilled water and acetone 3 time each. 0.19 g of dried product was obtained. This reflects only the reactivity of hydroxyl groups on the crystal surface. Isocyanates or diisocyanates were shown to react with the methylol groups of copolymers under similar reaction conditions at a higher temperature of 170 °C in DMSO.

2.2.6. Reactions of acrylate double bonds

(a) Free radical polymerization of monomer EMADO

A 100 ml round bottom flask with magnetic stirrer was charged with 1.0 g of monomer EMADO and 3 ml of cyclohexane as solvent. 15 mg of AIBN was added at the temperature of 65 °C. The reaction was carried out for 24 hrs. The free radical polymer was precipitated in methanol then filtered and dried. 0.15 g of light yellow solid was collected.

(b) Thermal polymerization of monomer EMADO

A drop of monomer EMADO and 20 drops of DMSO-d_6 was added in a 5 mm NMR tube and heated to 170 °C for 2 hrs in an oil bath. The resulting content was used for NMR observation of the possible thermal polymerization of monomer EMADO.

(c) Model reaction of monomer EMADO in base hydrolysis condition

A drop of monomer EMADO and 10 drops base hydrolysis solution (see section 2.2.4.) was added in a NMR tube and heated to 170 °C for 1 hr. The reaction mixture was then used for NMR determination.

(d) Model reaction of monomer EMADO with dodecylamine

A model reaction of monomer EMADO (1 drop) with dodecylamine (1 drop) in 30 drops of DMSO-d_6 as solvent in a test tube was carried out at room temperatures for 24 hrs under stirring. The reaction mixture was then used to ascertain the reactivity of acrylate double bond with dodecylamine.

(e) Model reaction of monomer EMADO with polyamide

0.2 g of polyamide and 0.2 g of monomer EMADO were added in a test tube with 2 ml of DMSO as solvent. The reaction was performed at 170 °C for 1 hr under magnetic stirring. The reaction mixture was cooled to room temperature to precipitate the polyamide. The polyamide was collected by filtration and washed with acetone then dried at 45 °C under vacuum. The polyamide used had a molecular weight of 25 x 10^3 and its carboxyl end groups were capped with phenethylamine in DMSO at 170°C for 5 hrs.

(f) Reaction of copolymers with dodecylamine

Reaction of copolymer (0.5 g) with dodecylamine (0.2 g) was carried out in DMSO (5ml) at 170 °C for 30 minutes in a round bottom flask with magnetic stirrer. About 10 mg of hydroquinone was added to the solution to prevent the free radical reaction of double bond. The reaction mixture was cooled to room temperature and the reacted copolymer was collected as light yellow solid by filtration. The product was then washed with acetone 3 times and dried at 45 °C under vacuum. The yield of reaction was about 85%.

(g) Reaction of copolymers with polyamide

A graft reaction of copolymer (0.5 g) with polyamide (0.5 g) was performed in DMSO (5 ml) at 170 °C for 2 hrs. About 10 mg of hydroquinone was added to the solution to prevent the free radical crosslinking of double bond. The carboxyl end group of the polyamide used was capped at 170 °C for 5 hrs with phenethylamine. The polyamide can be dissolved in DMSO at temperature higher than 50 °C. The reaction mixture after reaction was filtered at 80-90 °C to removed the unreacted polyamide and washed with hot DMSO at

90 °C three times to completely remove the unreacted polyamide. Then the graft copolymer was dried at 45 °C under vacuum. The yield of the reaction was about 70%.

2.2.7. NMR characterization of comonomers and copolymers

All NMR spectra were obtained on an IBM 200-SY NMR spectrometer operating at 200 MHz for proton using Bruker software. The chemical shifts were referenced to tetramethylsilane at 0 ppm for ^{1}H spectra and DMSO-d_6 at 39.5 ppm for ^{13}C spectra. A distortionless enhanced polarization transfer (DEPT) ^{13}C spectrum was obtained to identify the CH and CH_2 groups using Bruker software. The 90° pulse width for solvent DMSO-d_6 was determined as 16.0 μs for ^{1}H and 15.0 μs for ^{13}C.

2.2.8. Determination of molecular weight of copolymers

The molecular weight of the copolymer was estimated from the inherent viscosity of copolymer-hexafluoroisopropanol (HFIP) solution at 25 °C with a concentration of 0.200 g/dl. The inherent viscosity was compared with that of ethylene oxide-trioxane copolymer with 1.4 mole % incorporation and a large range of molecular weight. All mole percents in the present work are based on formaldehyde as a common unit. The molecular weight of copolymers was also estimated from the polymer end group analysis from NMR data.

2.2.9. Thermal analysis of copolymers - crystallinity and thermal stability

The crystallinity of copolymer was determined by DSC technique with a DuPont Thermal Analyzer, Model 2100. All the samples used were dissolved in the base hydrolysis solution at 170-175 °C and then crystallized as the solution cooled to room temperature. The sample, 2-4 mg, was sealed in a DSC hermetic cell and heated at the rate of 10 °C/min. from the equilibrium temperature of 55 °C to 185 °C under nitrogen purging at the rate of 50 ml/min.. The sample was then allowed to slowly cooled to 55 °C and recrystallized from the melt in the DSC cell. No cooling accessory was used. The sample was reweighed after analysis to determine whether any of the sample had volatilized and escaped from the sealed DSC cell during the first run. The crystallinity from the melt of the sample was analyzed from 55 °C to 185 °C for the second run. The data were processed using a TA DSC program to determine the heat of fusion and crystallinity of copolymers. The integration of endotherm is based on the assumption of a sigmoidal baseline derived from tangent baselines at peak start and end. Percent crystallinity was based on a ΔH_f equal to 245.4 J/g for 100% crystallinity[8]. The effect of comonomer units on ΔH_f was assumed to be negligible. The temperature and heat of fusion were calibrated by using a weighed indium sample.

The thermal stability of copolymer was determined by TGA techniques with a DuPont Thermal Analyzer, Model 990.

The sample size of copolymers was 2-4 mg. The heating rate was 10 °C/min. from 60 to 300 °C under the atmosphere of nitrogen.

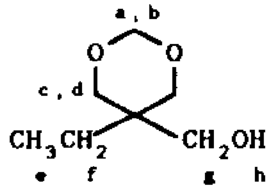
2.2.10. Determination of water contents in monomers

The water contents of trioxane and EHMDO were determined by using Karl-Fischer (Aquametry) method with the "dead-stop" technique. Titrater used was an Aquametry II Apparatus from J.T. Baker Co.

2.3. Results and Discussion

2.3.1. Synthesis of 5-ethyl-5-hydroxymethyl-1,3-dioxane (EHMDO)

Fig. 2-1 shows a ^{1}H NMR spectrum for EHMDO at 120 °C in DMSO-d_6. The protons of methylene groups in the ring are



inequivalent. Protons, **a** and **b**, form an AB systems and have a four line absorption at 4.6 - 4.8 ppm; protons, **c** and **d**, also form an AB system at 3.4 - 3.7 ppm. A triplet at 0.82 ppm is due to the methyl protons **e** coupled with methylene protons **f**. A quartet at 1.35 ppm is due to methylene protons **f**. A singlet at 3.43 ppm is due to the methylene proton **g**.

2.3.2. Syntheses of 5-ethyl-5-methylacrylate-1,3-dioxane (EMADO)

Fig. 2-2 shows a ^{1}H NMR spectrum for comonomer 5-ethyl-5-methylacrylate-1,3-dioxane (EMADO) at 120 °C in DMSO-d_6. As in EHMDO, the protons of methylene groups (**a**, **b** and **c**, **d**) of the ring are inequivalent and form two set of AB systems similar with comonomer EHMDO, protons **c**, **d** shift appears 0.06 and 0.07 ppm downfield respectively

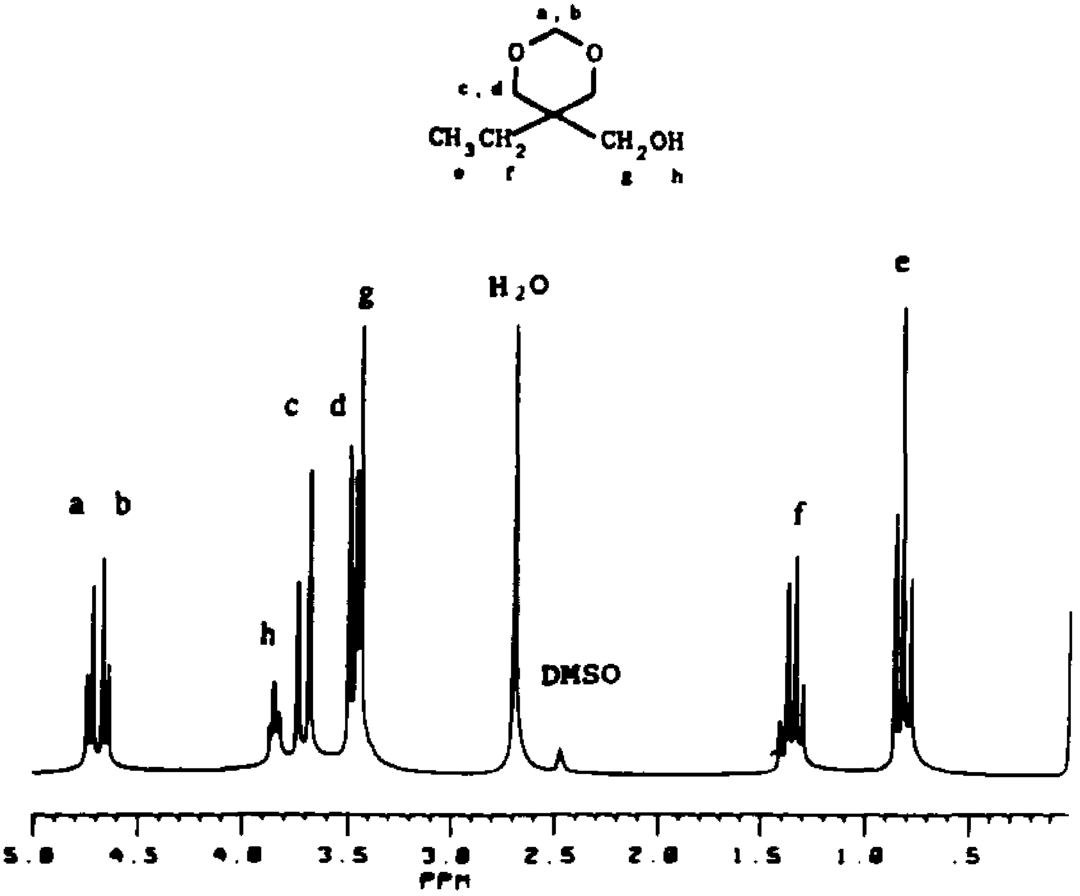


Fig. 2-1 ^1H NMR spectrum of 5-ethyl-5-hydroxymethyl-1,3-dioxane in DMSO-d_6 at 120 °C.

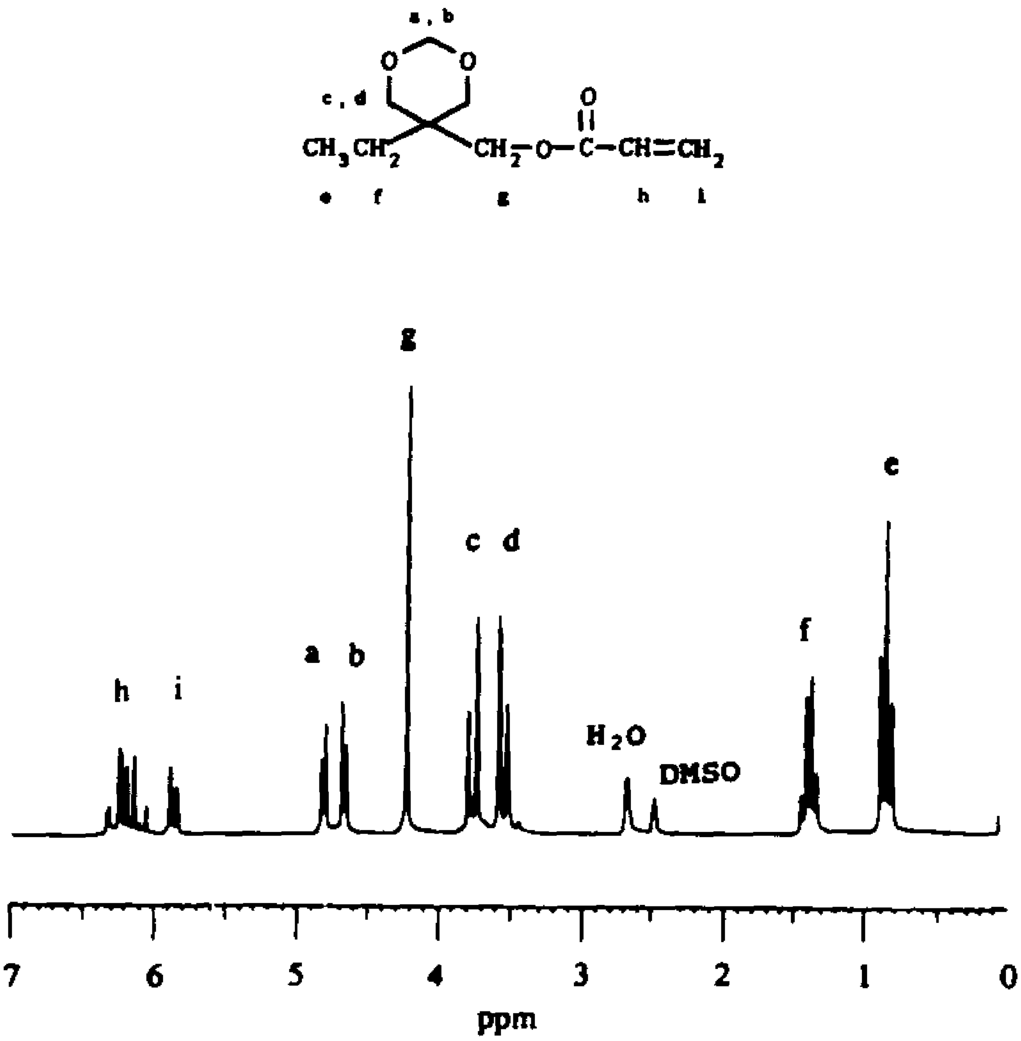
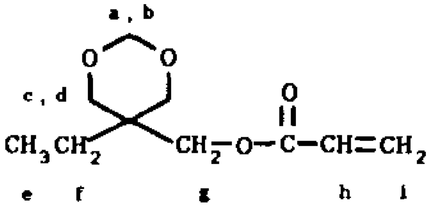


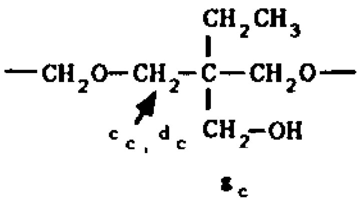
Fig. 2-2 ^{1}H NMR spectrum of 5-ethyl-5-methylacrylate-1,3-dioxane in DMSO-d_6 at 120 °C.

to comonomer EHMDO due to the acrylate group. A multiplet at 5.84-6.40 ppm is due to its protons of double bond (**h**, **i**). A singlet at 4.21 ppm is due to protons **g** of methylene group linked with the ester group. A triplet at 0.82 ppm and a quartet at 1.36 ppm are due to the protons of methyl group (**e**) and methylene group (**f**) respectively.



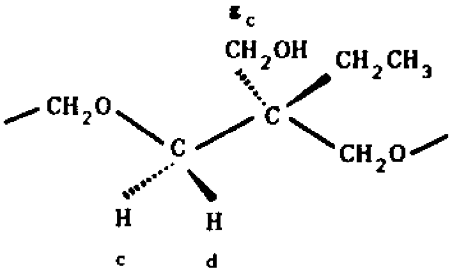
2.3.3. Copolymerization of trioxane with 5-ethyl-5-hydroxymethyl-1,3-dioxane

EHMDO as a thermodynamically stable six member ring does not undergo ring opening homopolymerization. Due to its hydroxyl group, it is expected to be an efficient chain transfer agent in cationic processes. The homopolymer of EHMDO could not be obtained under the conditions of $BF_3 \cdot OEt_2$ as initiator at 65 °C for a reaction time up to a week. However, its cationic ring opening copolymerization with trioxane in the bulk as well as in solution was established in the present work. A ^1H NMR spectrum of the copolymer is shown in Fig. 2-3. The presence of absorptions **e**, **f**, **c** and **d**, confirms the incorporation of EHMDO in the copolymer. A number of structural units due to comonomer incorporations are possible. Ring opening copolymerization of EHMDO gives the structure:

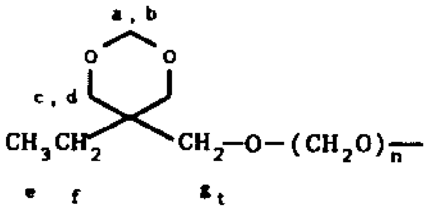


$$-CH_2O-CH_2-\overset{CH_2CH_3}{\underset{CH_2-OH}{C}}-CH_2O-$$

Protons c_c and d_c of the copolymer are inequivalent due to the lack of a plane symmetry element in this unit as in the comonomer:



Hence, protons c_c, d_c form an AB system and show a 4-line absorption. Cationic chain transfer due to EHMDO leads to the structure:



In this case, the protons a, b, e and f should have almost the same chemical shifts as in the monomer, and

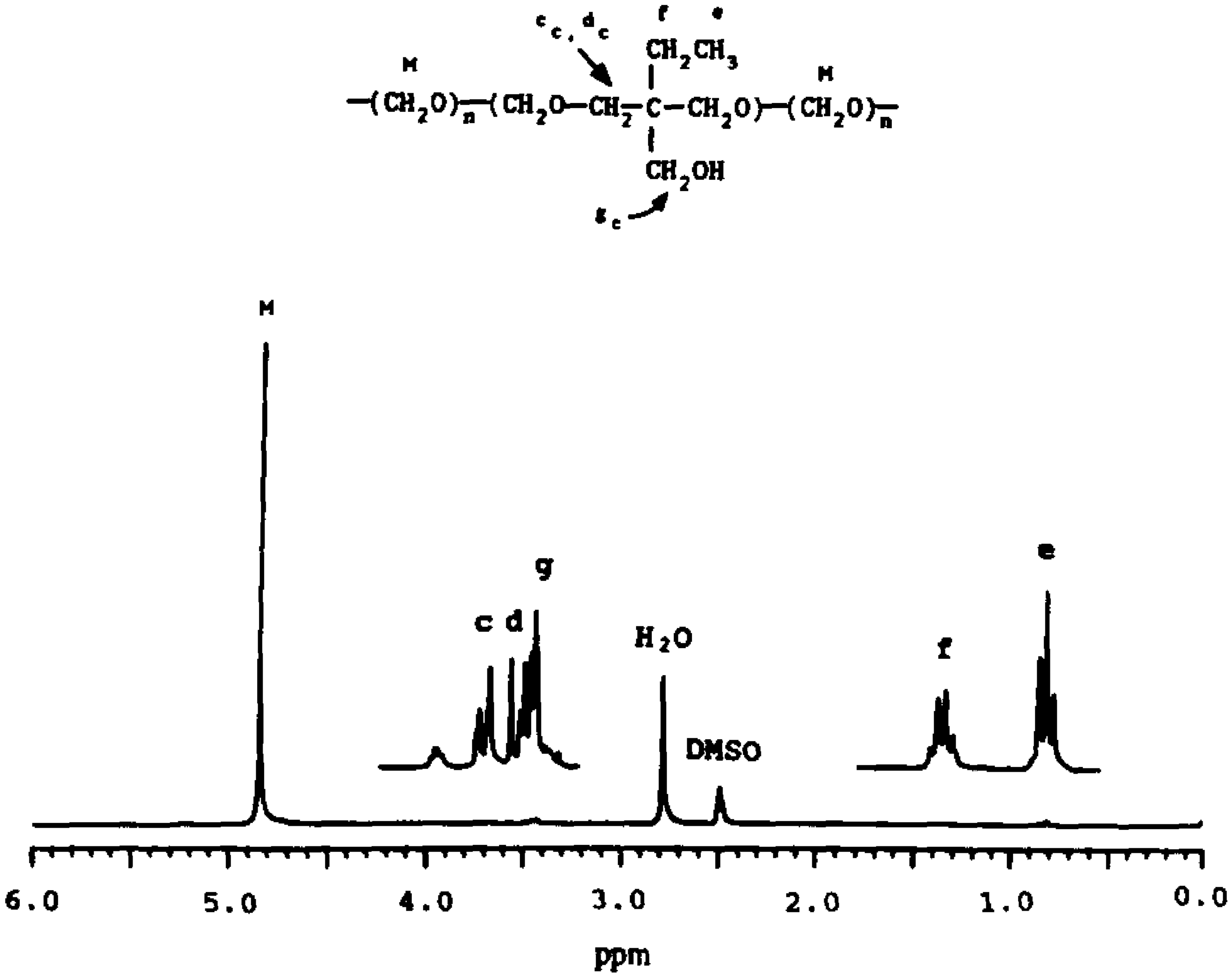
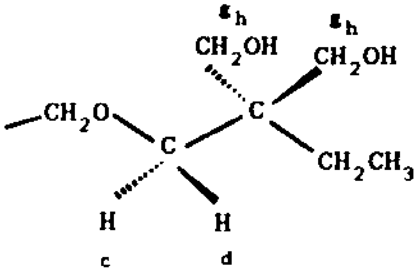


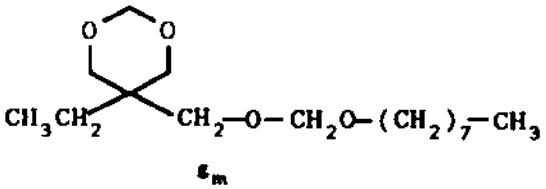
Fig. 2-3 ^1H NMR spectrum of copolymer of trioxane with 5-ethyl-5-hydroxymethyl-1,3-dioxane in DMSO-d_6 at 120°C.

protons c and d still constitute an AB system. But the proton g absorption shifts to a lower field due to the conversion of the hydroxyl group to an ether group linked to $-(CH_2O)_n-$. Base hydrolysis to remove the unstable end groups leads to the formation of the end group:



Here, the protons, c and d, are equivalent and show a singlet absorption, c_h.

^{1}H NMR spectra in Fig. 2-4 illustrate in detail absorption for the region of 3.2 to 4.0 ppm for the monomer EHMDO and the copolymers obtained from solution and bulk copolymerization. The protons g absorption, a singlet at 3.43 ppm in monomer, shifts to 3.55 ppm when the monomer units incorporated as a chain transfer end group. A model compound



was synthesized to confirm this assignment. In this model compound, g shifts from 3.43 to 3.50 ppm (g_m). If the

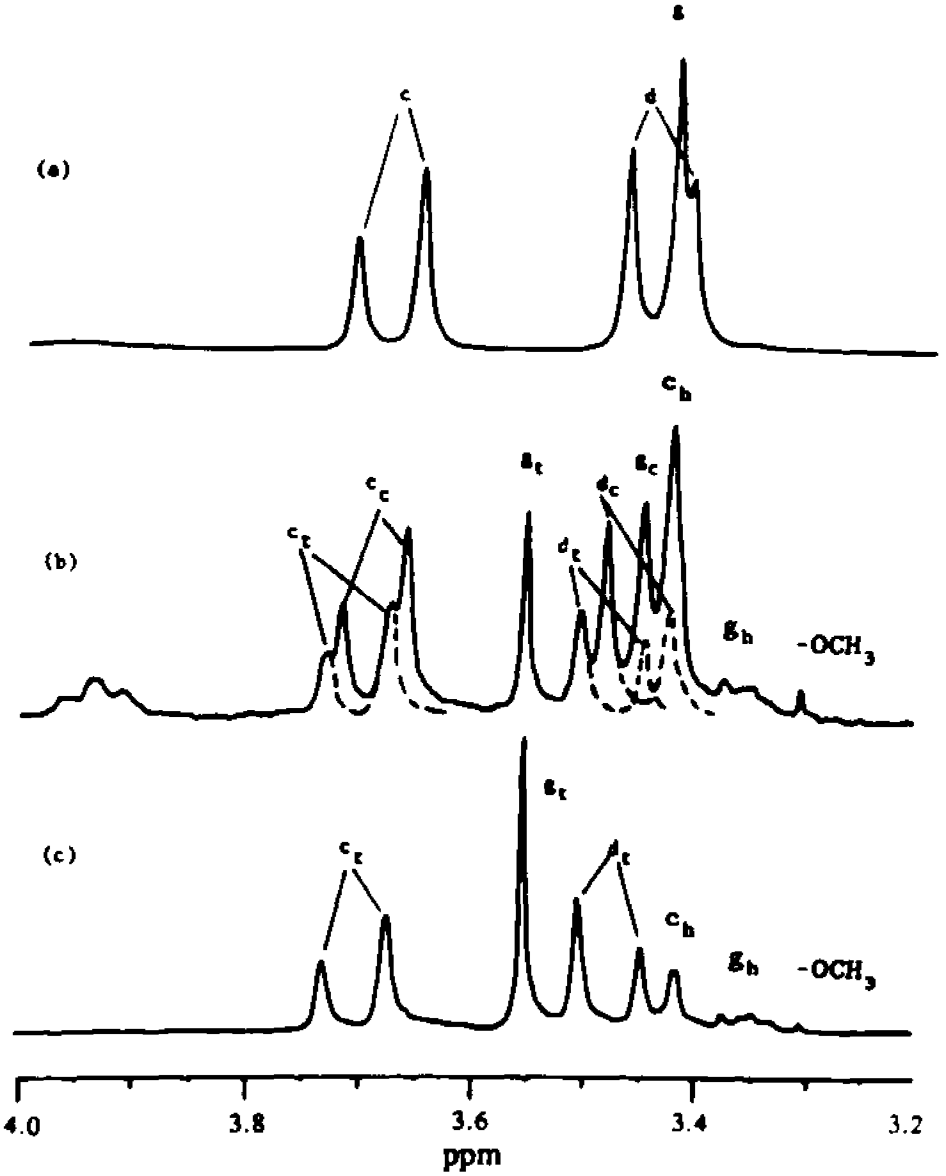


Fig. 2-4 Portion of ^{1}H NMR spectra of copolymer of trioxane with 5-ethyl-5-hydroxymethyl-1,3-dioxane and monomer in DMSO-d_6 at 120 °C.

(a) Monomer

(b) Copolymer from solution copolymerization

(c) Copolymer from bulk copolymerization methylene oxide connected to the tertiary carbon is linked further to a number of methylene oxide groups $-(CH_2O)_n-$ as in the copolymer, **g** should shift further downfield. Fig. 2-4(c) is a ^1H NMR spectrum of copolymer obtained from bulk copolymerization. A singlet, g_t, at 3.55 ppm and a four line absorption, c_t and d_t, indicate a chain transfer end group in the copolymer. A doublet, g_h at 3.37 ppm is due to the methylene protons of the two methylol groups. A singlet, c_h, at 3.42 ppm is due to the two equivalent protons of methylene oxide group connected to the tertiary carbon. A singlet at 3.31 ppm is from methoxy end group originating from hydride transfer[9]. Fig. 2-4(b) shows a ^1H NMR spectrum of copolymer obtained from solution copolymerization, a more involved spectrum than that of bulk copolymer. The chain transfer end group (g_t, c_t and d_t) and hydrolysis end group (g_h and c_h) can be observed clearly, although some absorption overlap as indicated by dash lines. For structural unit from ring opening process, a second 4 line absorption, c_c and d_c was observed and **g** shifted to 3.45 ppm (g_c).

Based on the analysis of the ^1H NMR data above, the structure of copolymer can be depicted as follows:

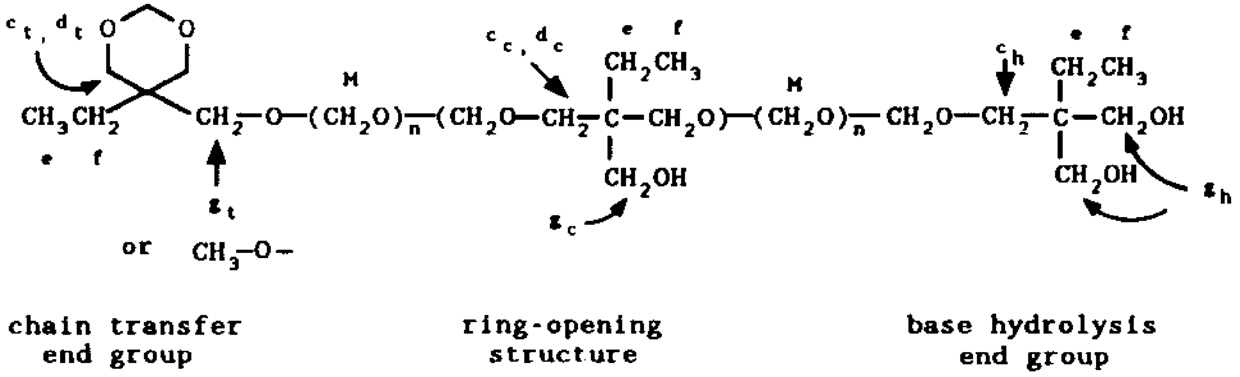


Table 2-1 summarizes data from copolymerization experiment.

Table 2-1 Copolymerization of trioxane with EHMDO in bulk and solution

Sample No.	Monomers				Cyclohexane	BF_3Et_2O		Yield (wt.%)		Copolymer			
	Trioxane		EHMDO					Before Hydro.	After Hydro.	mol% Feed	EHMDO Incorp.	$MWx10^{-3}$	
	g	mmol	g	mmol	ml	µl	mmol					(a)	(b)
2-08	19.0	211	1.0	6.8	/	25	0.20	96	26	1.1	1.0	4	7
1-95	16.0	178	4.0	27	/	25	0.20	62	/	4.8	2.4	2	/
2-142	20.5	228	0.5	3.4	20	40	0.33	/	34	0.6	1.2	5	9
2-125	19.0	211	1.0	6.8	25	60	0.49	98	44	1.1	1.2	4	/
3-07	42.1	467	5.0	34	40	300	2.44	91	33	2.4	1.4	3	8
2-132	17.0	189	3.0	21	20	280	2.28	82	28	3.6	3.6	3	/

Feed: Based on trioxane, $C_3H_6O_3$
Incorp.: Based on formaldehyde, CH_2O
(a) From NMR
(b) Estimated from viscosity

The yields after base hydrolysis are in general low, i.e. 26-44%. The molecular weight of copolymer was estimated from viscosity determination and NMR end group analysis. Assuming every copolymer chain has a chain transfer end group, the peaks g_t and $-OCH_3$ can be used to estimate the molecular weight of copolymer:

$$\overline{M}_n = \frac{\text{Area of main peak (M)/2}}{\text{Area of end group } (g_t)/2 + \text{Area of OCH}_3/3} \times 30$$

It is apparent that the molecular weight of ca. 2×10^3 - 5×10^3, obtained from end group calculation is quite low. The molecular weight decreases as the feed of EHMDO increases. This is consistent with EHMDO being an efficient chain transfer agent. The incorporation of EHMDO in copolymer is about 1.0~3.6 mole%, based on the formaldehyde unit, for feeds of 1.1~3.6 mole% based on trioxane. It can be calculated using equation below:

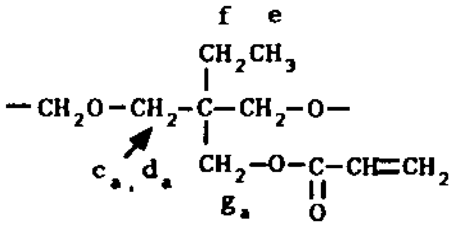
$$\text{Incorp. mole\%} = \frac{\text{Area of peak e/3}}{\text{Area of peak (e/3 + M/2)}}$$

The incorporation of EHMDO is only one to two units of EHMDO in one molecular chain in addition to the end group. However, it is clearly established that EHMDO can undergo ring opening copolymerization with trioxane. For the solution copolymerization polymer, the peaks c_c, c_t, d_c, d_t, c_h and g_c, g_t, g_h are observed readily in the ^{1}H NMR spectrum (Fig. 2-4(b)). In the case of bulk copolymerization polymer, only the peaks of c_t, d_t, c_h and g_t, c_h, g_h due to the end groups are observed (Fig.2-4(c)); peaks of c_c, d_c, and g_c due to ring opening of EHMDO are absent. Apparently, the incorporation of EHMDO through ring opening is more difficult in the bulk than in the solution copolymerization.

2.3.4. Copolymerisation of trioxane with 5-ethyl-5-methylacrylate-1,3-dioxane, EMADO

A ^{1}H NMR spectrum of copolymer of trioxane with 5-ethyl-5-methylacrylate-1,3-dioxane (EMADO) in bulk copolymerization is shown in Fig. 2-5. The main peak at 4.84 ppm is due to the protons of $-(CH_2O)_n-$. The multiplet at 5.84-6.40 ppm is due to the protons of double bond from units of EMADO. The multiplets at 0.82 and 1.36 ppm due to the methyl and methylene protons are observed. It is clear that EMADO is copolymerized with trioxane.

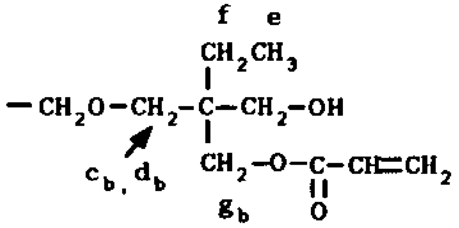
A number of structural units due to EMADO incorporation are possible. Chemical shift of proton "g" of the methylene unit connected to the ester linkage are different in different structural units. This proton is designated as key proton in ascertaining ring opening polymerization and identities of the ester groups. Ring opening copolymerization of EMADO gives the structure unit (A). Key proton g_a absorption shifts slightly upfield from 4.21 ppm in EMADO to 4.08 ppm in the copolymer. After base hydrolysis to remove unstable end segment, structure unit (A) becomes an end group, i.e. structure unit (B).



$-CH_2O-CH_2-\underset{CH_2-O-\underset{\|O}{C}-CH=CH_2}{\overset{CH_2CH_3}{C}}-CH_2-O-$

4.08 ppm

Structure unit (A)



$-CH_2O-CH_2-\underset{CH_2-O-\underset{\|O}{C}-CH=CH_2}{\overset{CH_2CH_3}{C}}-CH_2-OH$

4.06 ppm

Structure unit (B)

Key proton g_b is located at 4.06 ppm. The assignment of chemical shift for protons g_a and g_b is in line with the observation that as molecular weight of the copolymer decreases, the intensity ratio g_b/g_a increases. Protons c_a, and d_a are not equivalent and form an AB system, designated as **c**, **d** in Fig. 2-5 and 2-8(b). The pair, c_b, d_b shows same spectral characteristics.

Vinyl double bond and acrylate double bond were demonstrated to be polymerized in cationic polymerization or copolymerization[4,5,10]. In this work, cationic copolymerization of acrylate double bond was observed. Some of the nascent copolymers can not be completely dissolved in hexafluoroisopropanol, a good solvent for polyacetal copolymer at room temperature. The insoluble part of copolymer also can not be dissolved in DMSO at 170 °C. This insoluble portion is considered as crosslinked copolymer resulting from the opening of the dioxane ring as well as the acrylate double bond. A homopolymerization of EMADO (1.5 ml) was performed in the presence of $BF_3 \cdot Et_2O$ (8 μl) at

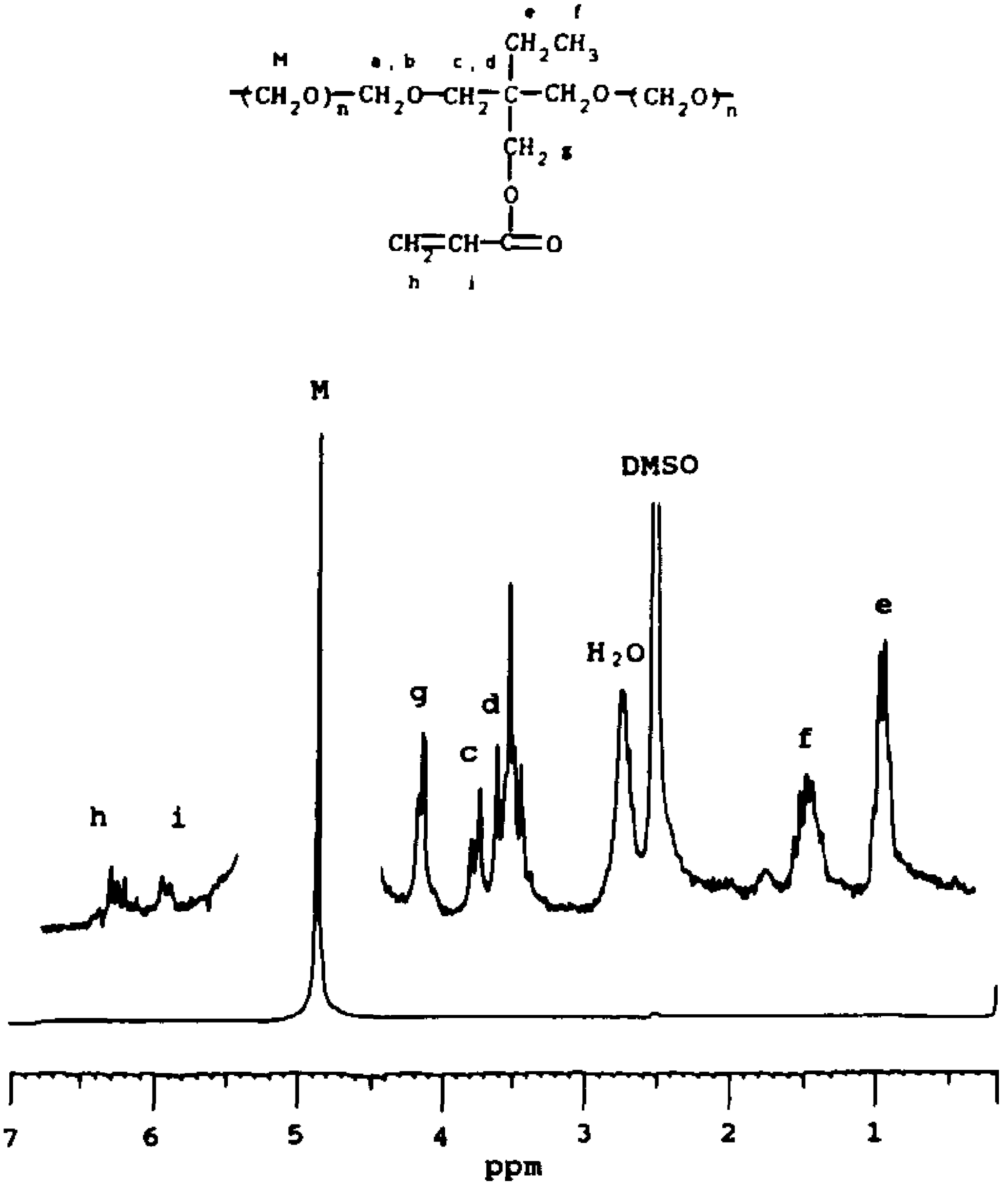
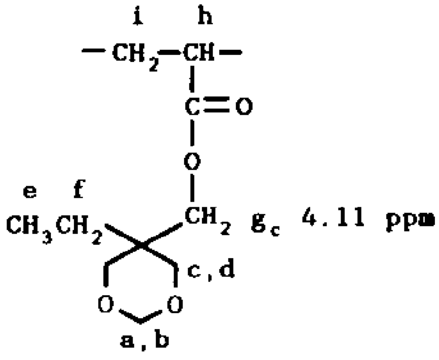


Fig. 2-5 ^{1}H NMR spectrum of copolymer of trioxane with 5-ethyl-5-methylacrylate-1,3-dioxane from bulk copolymerization in DMSO-d_6 at 120 °C.

room temperature in cyclohexane (1.5 ml) for 1 week. A light yellow, soft and crosslink polymer was found, due to the opening of both the double bond and the dioxane ring of EMADO.

The cationic copolymerization through double bond of EMADO gives structure unit (C):



Structure unit (C)

A model for free radical polymerization of EMADO was performed, resulting in a homopolymer with the repeat unit (C). Fig. 2-6 shows a ^1H NMR spectrum of homopolymer of EMADO. Absorption of key proton g_c shifts from 4.21 ppm in monomer to 4.11 ppm in polymer; absorption of proton i shifts from 6.3 to 1.70 ppm. This structure unit (C) is also observed in the copolymer as shown in Fig. 2-5. The peaks at 4.11 due to proton g_c and 1.70 ppm due to proton i were observed.

Hydrolysis of ester groups of structure unit (A) and (B) gives structure units (D) and (E) respectively:

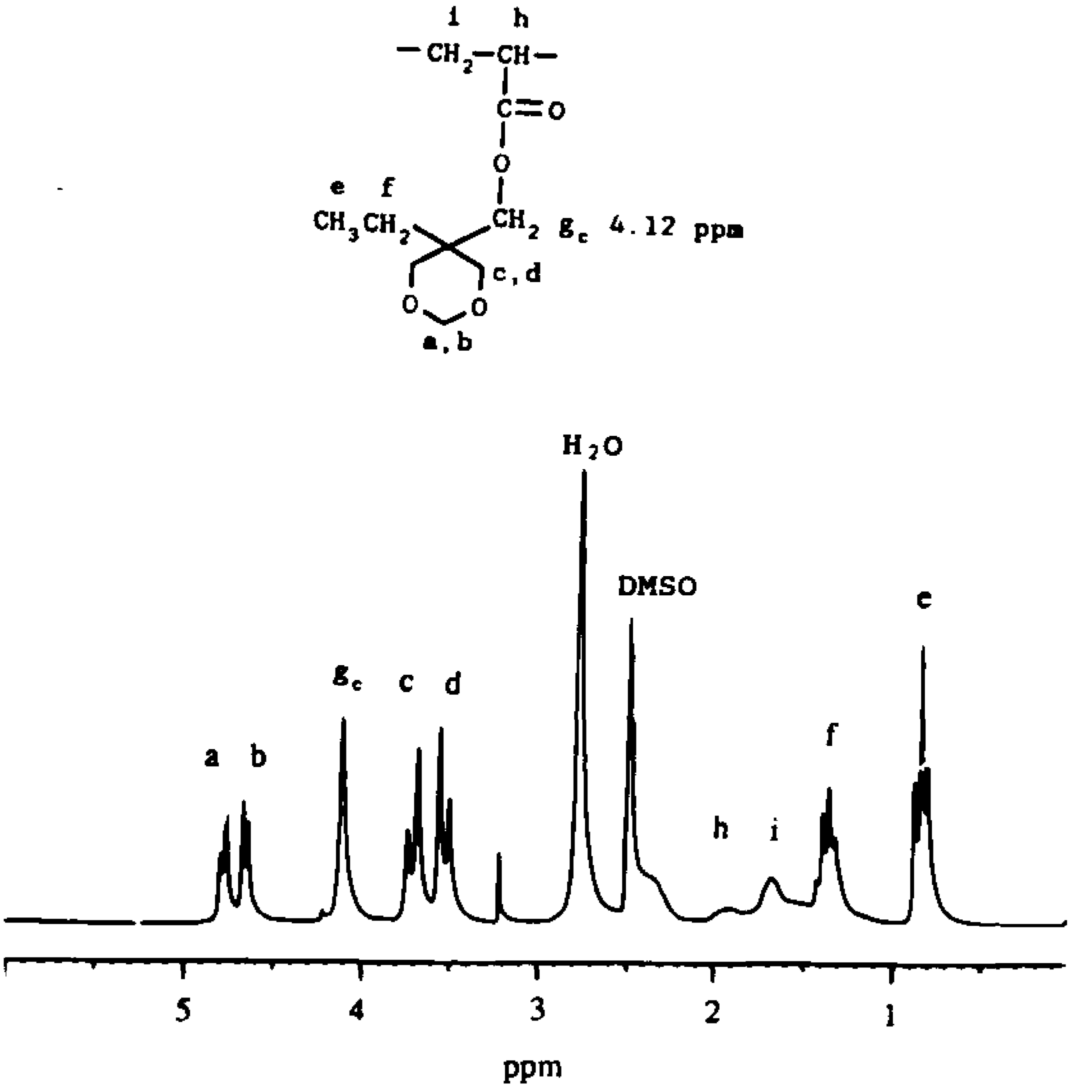
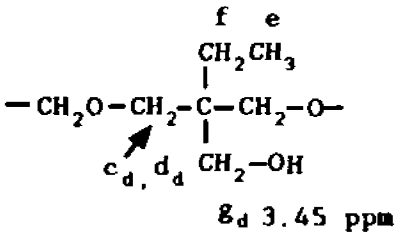
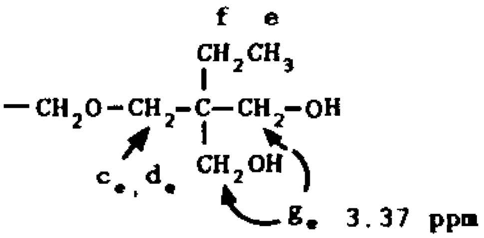


Fig. 2-6 ^{1}H NMR spectrum of free radical homopolymer of 5-ethyl-5-methylacrylate-1,3-dioxane in DMSO-d_6 at 120 °C.



Structure unit (D)



Structure unit (E)

These structure units also exist in copolymer EHMDO (Fig. 2-4). Absorptions of structure (D) can be observed in Fig. 2-7, a ^{1}H NMR spectrum of copolymer from solution copolymerization. A four line absorption of AB system at 3.42 to 3.73 ppm is due to protons c_d and d_d, with one line overlapping with g_d. Absorption of key protons g_d was split by the hydroxyl group into a doublet (3.42 and 3.47 ppm) in this case. Structural features of (A) and (B) are also observed in Fig. 2-7. Peaks at 4.08 and 4.06 ppm due to protons g_a and g_b are weak, corresponding to the low intensity of absorption protons **h** and **i** of double bond. For the AB system c_a and d_a, due to overlap, only one peak at 3.55 ppm can be observed. This indicates that the most of acrylate groups were hydrolyzed in the solution polymerization, perhaps due to acid generated by the BF_3 at high level. Protons of methyl group (**e**) and methylene group (**f**) in different structure units have slightly different chemical shift. Thus, multiplets due to methyl group (**e**) at 0.82 ppm and methylene (**f**) at 1.36 ppm are observed instead of clear triplets and quartets.

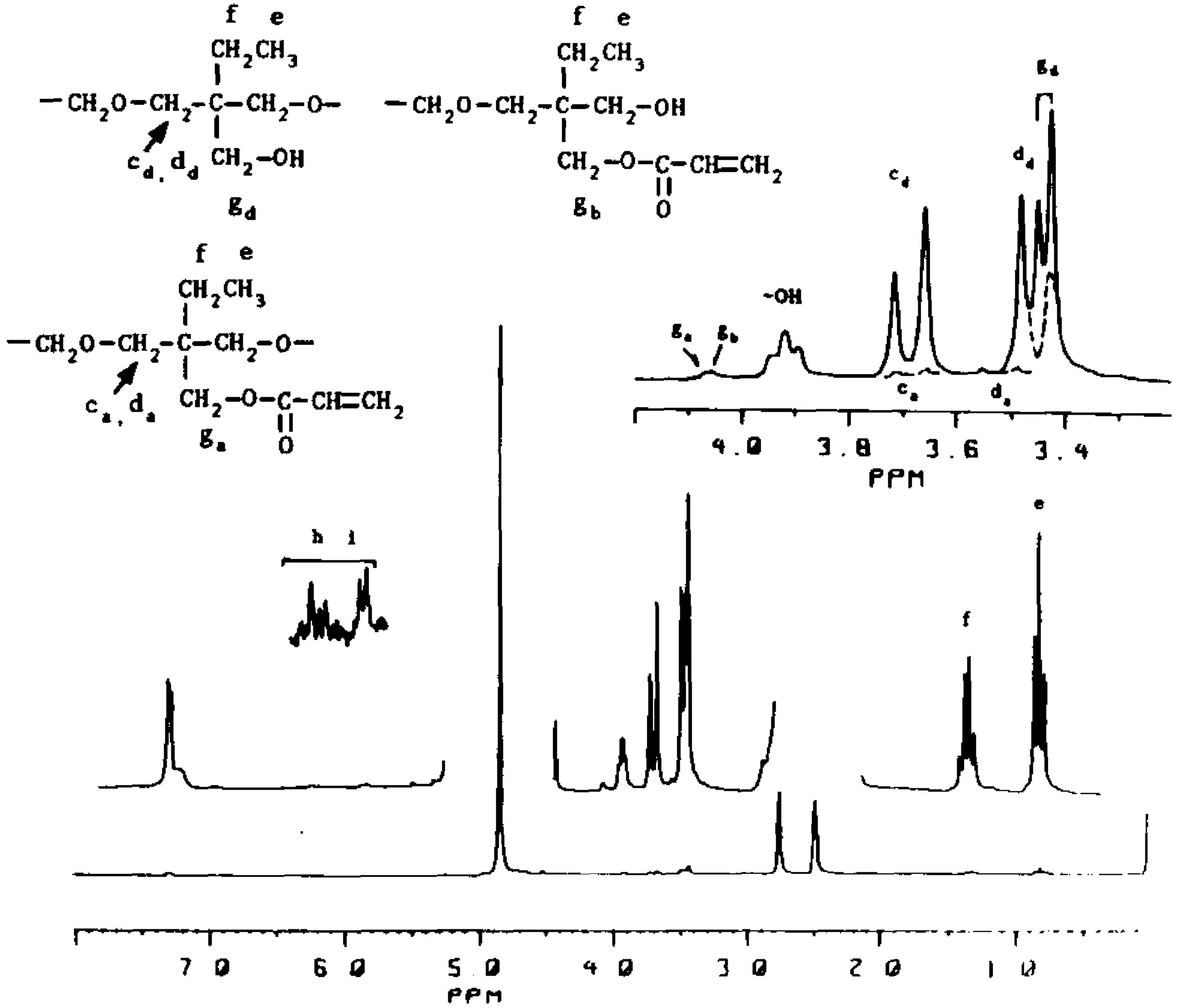
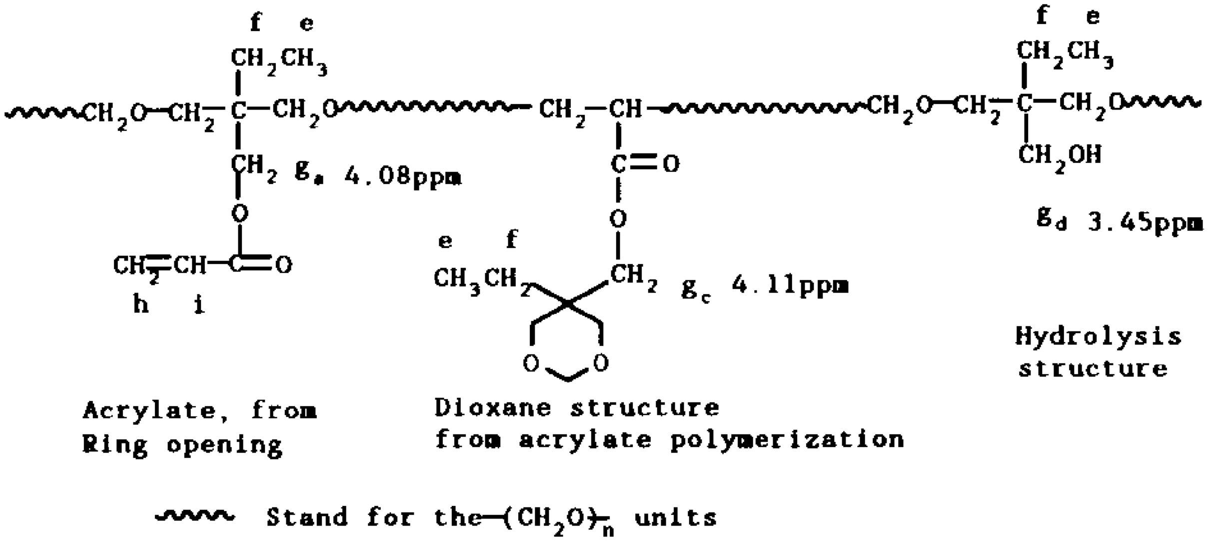


Fig. 2-7 ^1H NMR spectrum of copolymer of trioxane with 5-ethyl-5-methylacrylate-1,3-dioxane from solution copolymerization in DMSO-d_6 at 120 °C.

Fig. 2-8 shows detailed spectra information for copolymer from bulk and solution polymerization as well as EMADO in the region 3.20-4.30 ppm. For structure (E), $g_{\bullet}$ (3.37 ppm) now can be observed; $c_{\bullet}$ and $d_{\bullet}$ become a singlet at 3.43 ppm (compared with g_h and c_h in Fig. 2-4).

Based on the above analysis of structure units, the main structure of copolymer can be depicted as below:



The total incorporation of EMADO based on formaldehyde unit can be calculated from proton ● and the main peak of $(CH_2O)_n$ using equation below:

$$\text{Total Incorporation} = \frac{\text{Peak e/3}}{\text{Peak e/3 + main peak/2}} \quad (\text{mol \%})$$

The % of different structure units derived from EMADO can be estimated based on the following relationships:

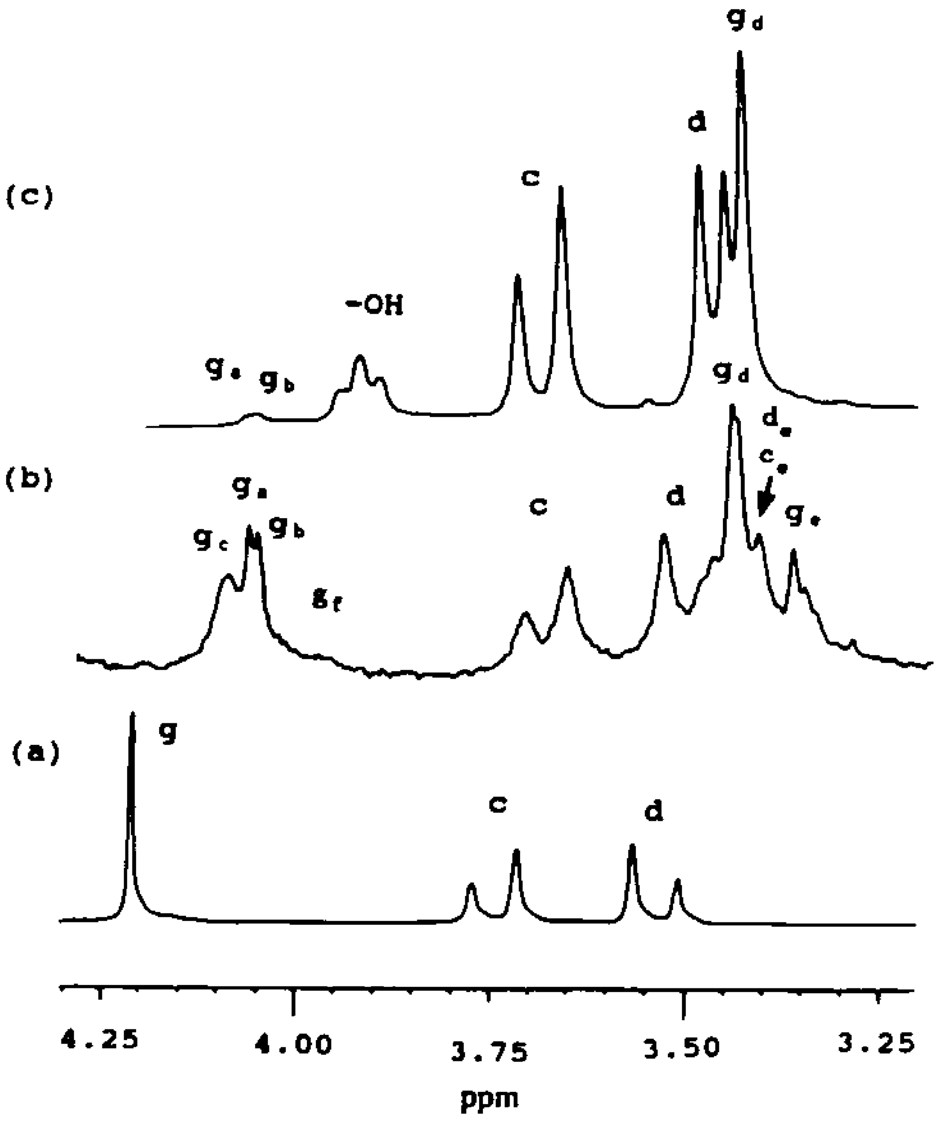


Fig. 2-8 Portion of ^1H NMR spectra of copolymer of trioxane with 5-ethyl-5-methyl-acrylate-1,3-dioxane and monomer in DMSO-d_6 at 120 °C.
(a) Monomer
(b) Copolymer from bulk copolymerization
(c) Copolymer from solution copolymerization

$$\text{Acrylate (A\%)} = \frac{\text{Peaks } (i + h)}{\text{Peak } e} \times 100\ (\%)$$

$$\text{Dioxane structure (D\%)}\ \frac{\text{Peak } g_c/2}{\text{Peak } e/3} \times 100\ (\%)$$

$$\text{Hydrolysis structure} = 100\% - A\% - D\% \quad (\%)$$

For sample Y-19, the mole % of the structure units are as follow:

Acrylate	0.60
Dioxane structure	0.13
Hydrolysis structure	0.25
Total incorporation	0.98

Table 2-2 summaries for copolymerization of TOX with EMADO.

Table 2-2 Copolymerization of TOX with EMADO

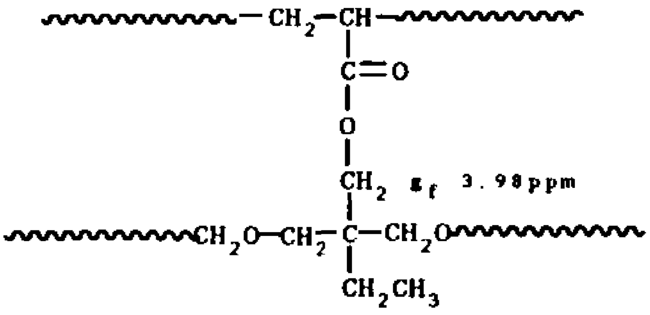
Sample No.	Feed mol%	Incorp. mol%	Yield* Wt%	Structure units (%) A & B	C	D & E	$MW \times 10^{-3}$	η_{inh} dl/g
Y-05	2.42	0.36	49.2	55.5	7.7	37.8	50	0.99
Y-03	4.20	0.86	34.3	42.8	30.1	27.1	46	0.95
Y-12	4.20	0.91	37.5	15.7	31.6	52.7	36	0.84
Y-08	4.30	0.97	43.3	17.5	47.8	34.7	53	1.03
Y-15	4.76	0.66	50.2	46.0	38.0	19.0	64	1.14
Y-18	10.1	1.19	38.3	44.9	29.2	25.9	17	0.60
Y-19	16.1	0.98	47.7	60.5	14.1	25.4	21	0.66
2-123	3.65	2.75	29.6	7.9	0	92.1	30	0.77
2-131	7.35	2.73	31.4	7.0	0	93.0	34	0.82
2-137	16.1	3.70	27.4	11.0	0	89.0	23	0.68

*From base hydrolysis.

**The top portion of the table is from bulk polymerization, the lower portion with three samples is from solution polymerization.

Structure units (A) and (B) with acrylate double bonds are desirable for further structural modification. In bulk copolymerization, mole % of structure unit A and B can be up to 60 % by mole. In solution copolymerization, structure (D) dominates. High concentration of initiator was used in solution polymerization. The resulting H^+ in high concentration can cause the hydrolysis of comonomer units in copolymer. Nevertheless, high molecular weight polyacetals with pendant hydroxyl groups was obtained.

Additional structure units in copolymer are possible. In the case of propagation through both double bond and the ring of the same monomer EMADO unit, a crosslink copolymer was formed:

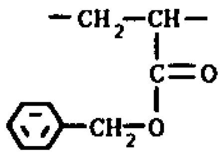


Absorption of key proton g at 4.21 ppm in monomer shifts to 4.08 ppm as the ring opens. If the double bond is saturated through addition of amine, the absorption of proton g will shift to 4.10 ppm (see section 2.3.6). In the case of crosslink, both the ring is open and the double bond is saturated, the absorption of proton g should shift further. The absorption of key proton g_f of the crosslink located at

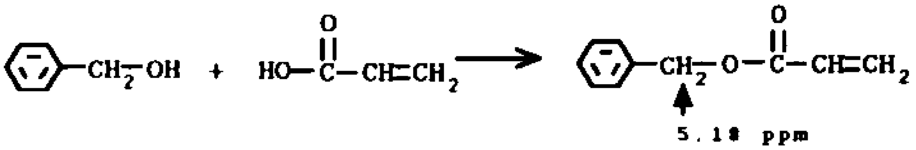
3.98 ppm was observed for a number of slightly crosslink samples.

The extent of crosslink depend on the level of incorporation of EMADO. The suppression of the crosslinking through acrylate double bond in copolymerization will be discussed in Section 3.

If the structure unit (C) was hydrolyzed in the polymerization in the same manner of structure unit (A), a pendant carboxyl group will be formed. In the process of base hydrolysis, benzyl alcohol is at high concentration level and can react with carboxyl group to form an ester group:



A model compound of benzyl acrylate was prepared.



The chemical shift of methylene next to the phenyl group is at 5.18 ppm (Fig. 2-9). A model reaction of acrylic acid with benzyl alcohol and DMF was performed at 170 °C for 1 hr as in the process of base hydrolysis of copolymer, the

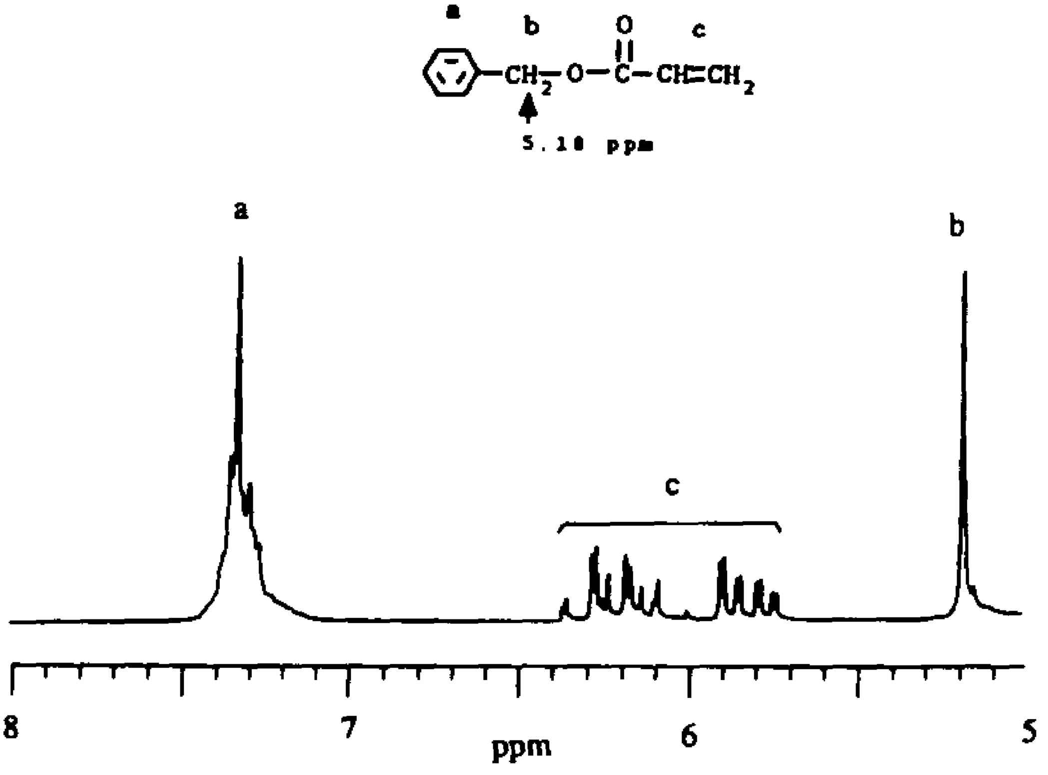


Fig. 2-9 ^{1}H NMR spectrum of benzyl acrylate in DMSO-d_6 at 120 °C.

resulting reaction mixture exhibits ^1H absorption at 5.18 ppm, indicating the occurrence of esterification. Some ^1H NMR spectra of the copolymers show an absorption at 7.30 ppm due to phenyl group, resulting from the esterification of benzyl alcohol with carboxyl groups of copolymer.

There are two possible side reactions in the base hydrolysis process, the polymerization of double bonds and the hydrolysis of ester groups. Fig. 2-10 is a ^1H NMR spectrum of monomer EMADO heated in DMSO-d_6 at 160 °C for 2 hrs. The absorption of double bond at 5.84-6.40 ppm diminishes compared with the methyl group, indicating the polymerization of double bond. The two singlets at 4.21 ppm and 4.11 ppm, correspond to monomer before and after polymerization. A model reaction was performed by replacing copolymer with monomer EMADO under the same base hydrolysis condition. Fig. 2-11 shows a ^1H NMR spectrum of the reaction mixture. A singlet at 4.11 ppm was observed; 20 % of double bond was lost in comparison with the methyl groups, indicating the polymerization of double bonds. However the ratios of integration of the peaks g/f and (h+i)/e are equal, indicating that no ester groups were hydrolyzed. If the monomer EMADO were hydrolyzed, monomer EHMDO should had been formed. In this case, a peak at 3.43 ppm due to key proton g should be observed. In Fig. 2-11, no absorption appear at 3.43 ppm.

In some cases, insoluble crosslink copolymer particles were observed in the process of base hydrolysis. The

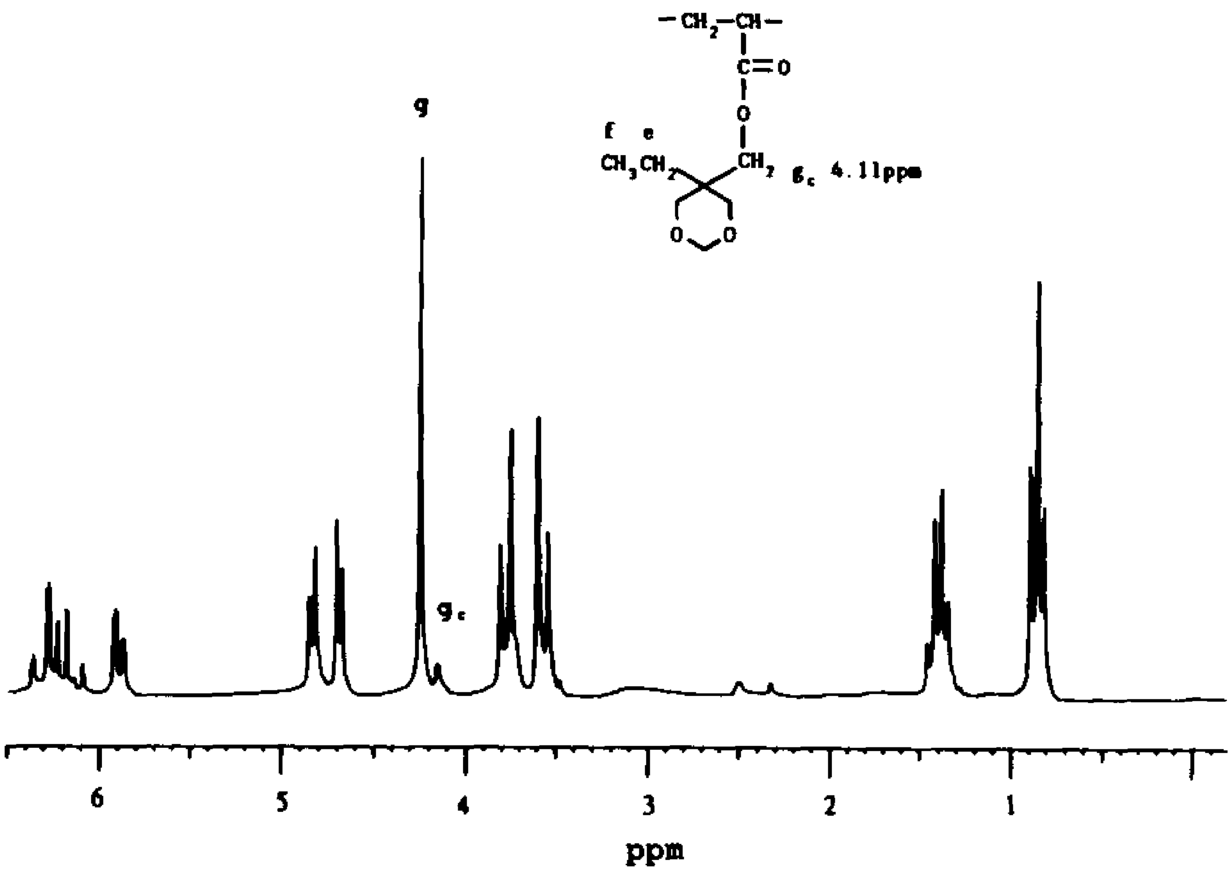


Fig. 2-10 ^{1}H NMR spectrum of 5-ethyl-5-methylacrylate-1,3-dioxane heated in DMSO-d_6 at 170°C for 2 hr.

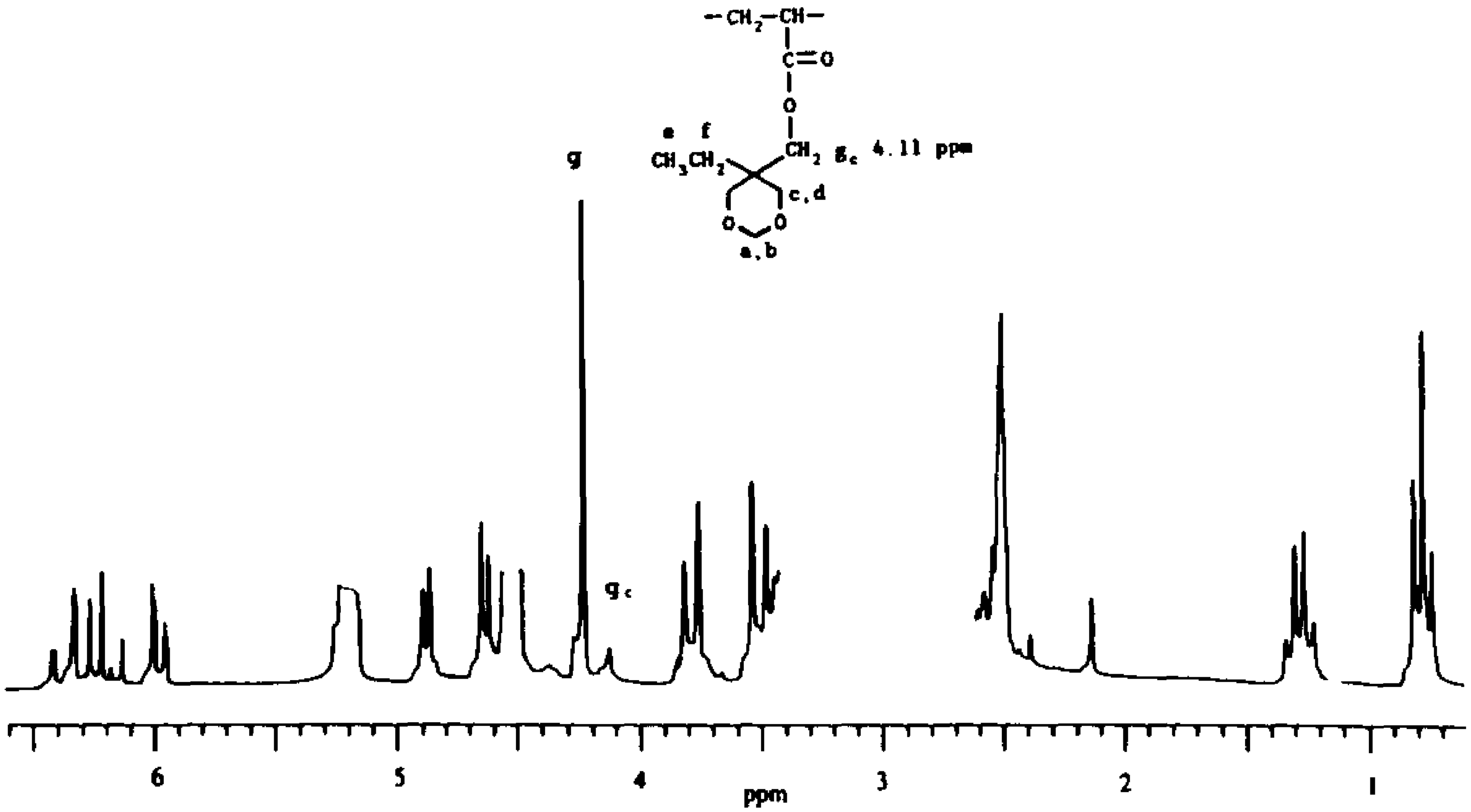
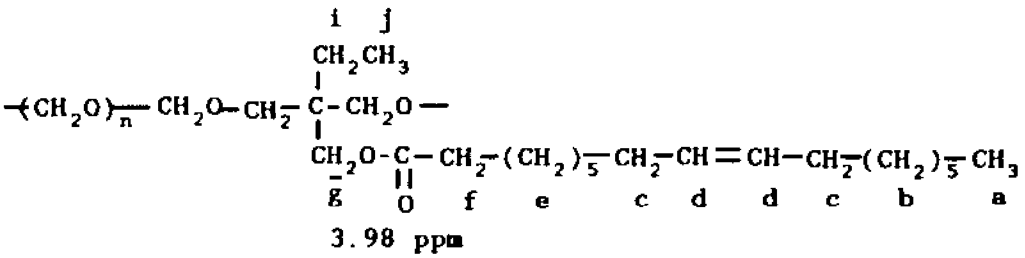


Fig. 2-11 ^{1}H NMR spectrum of 5-ethyl-5-methylacrylate-1,3-dioxane heated in base hydrolysis solution at 170°C for 1 hr.

addition of inhibitor, e.g. 0.1% hydroquinone suppressing crosslinking due to the radical processes.

2.3.5. Reaction of copolymers with hydroxyl groups

The reactivity of the hydroxyl functional group of the copolymer was demonstrated through the formation of graft and crosslink of copolymer. The copolymer reacted with olecyl chloride efficiently. The structure of graft copolymer is shown below:



$$-(CH_2O)_n-CH_2O-CH_2-\overset{\overset{CH_2CH_3}{|}}{\underset{\underset{CH_2O-\underset{\underset{O}{\|}}{C}-CH_2-(CH_2)_5-CH_2-CH=CH-CH_2-(CH_2)_5-CH_3}{|}}{C}}-CH_2O-$$

Fig. 2-12 shows a ^1H NMR spectrum of the reaction product. The pendant hydroxyl in copolymer reacted with acyl group, resulting in an ester group. The absorption of key proton g of ester group shifts from 3.45 ppm in copolymer (Fig. 2-4B) to 3.98 ppm. 56% of methylol group had reacted. Isocyanate is also reactive with hydroxyl group of copolymer EHMDO. Phenylisocyanate was demonstrated to be grafted in copolymer

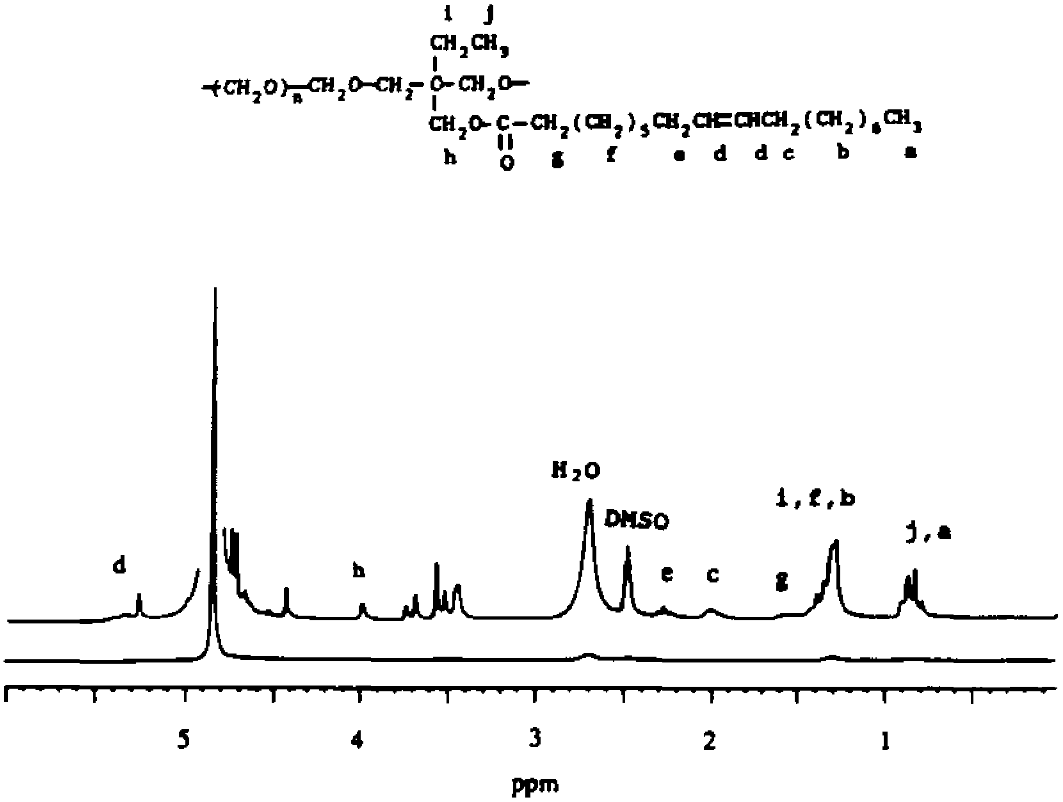
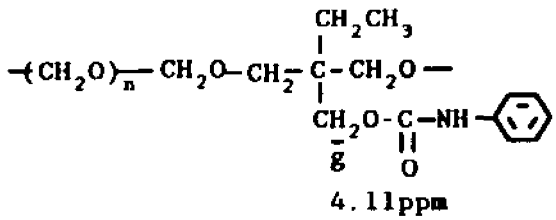


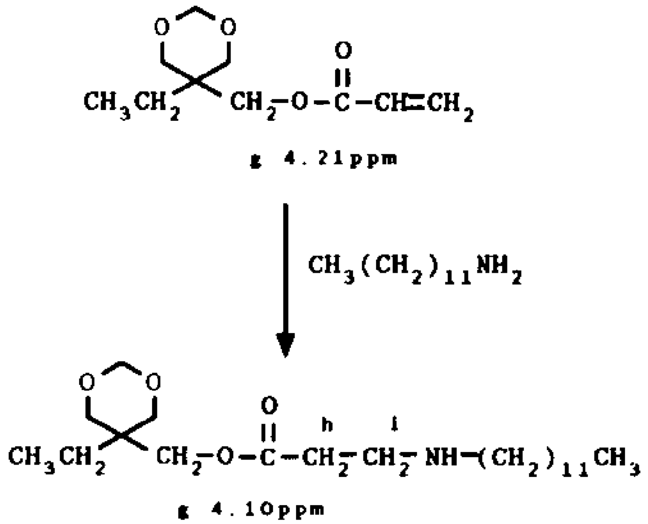
Fig. 2-12 ^{1}H NMR spectrum of copolymer of trioxane with 5-ethyl-5-hydroxymethyl-1,3-dioxane reacted with oleoyl chloride in DMSO-d_6 120 °C.



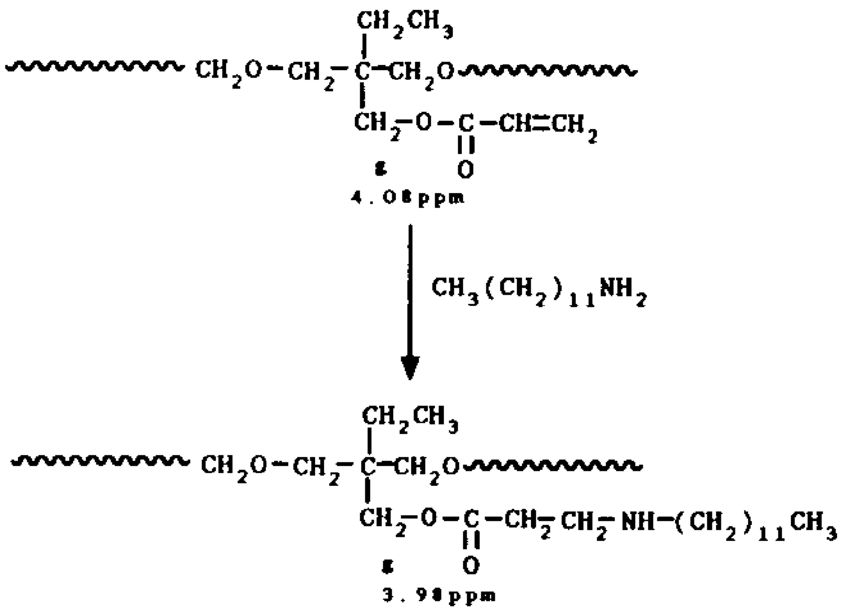
EHMDO as indicated by the absorption of proton **g** at 4.11 ppm. The use of phenyl diisocyanate caused an insoluble product.

2.3.6. Reaction of copolymers with acrylate groups

One of the applications of the pendant acrylate functionality is the synthesis of graft copolymers through addition of amino groups to the double bond, i.e. the Michael reaction. A polyamide, having one amino end group after its acid end group was capped, was selected for the graft reaction. First, a model reaction of dodecylamine with EMADO in equal mole ratio at room temperature was examined. Figure 2-13 shows a ^1H NMR spectrum and assignment of the reaction mixture resulting from reaction of EMADO with dodecylamine at room temperature for a day. The marked decrease in absorption at 5.84-6.40 ppm due to the double bond relative to the other peaks was indicative of a facile reaction. The new peaks **i** and **h** at 2.80 ppm and 2.55 ppm verify the amine addition to the double bond. The absorption of key protons **g** shifts to 4.10 ppm from 4.21 ppm.



Sample of copolymer EMADO was subjected to reaction with dodecylamine in DMSO at 170°C for 30 minutes. Fig. 2-14 shows a ^1H NMR spectrum of copolymer EMADO reacted with dodecylamine at 170 °C for 30 min. The key protons **g** shifts



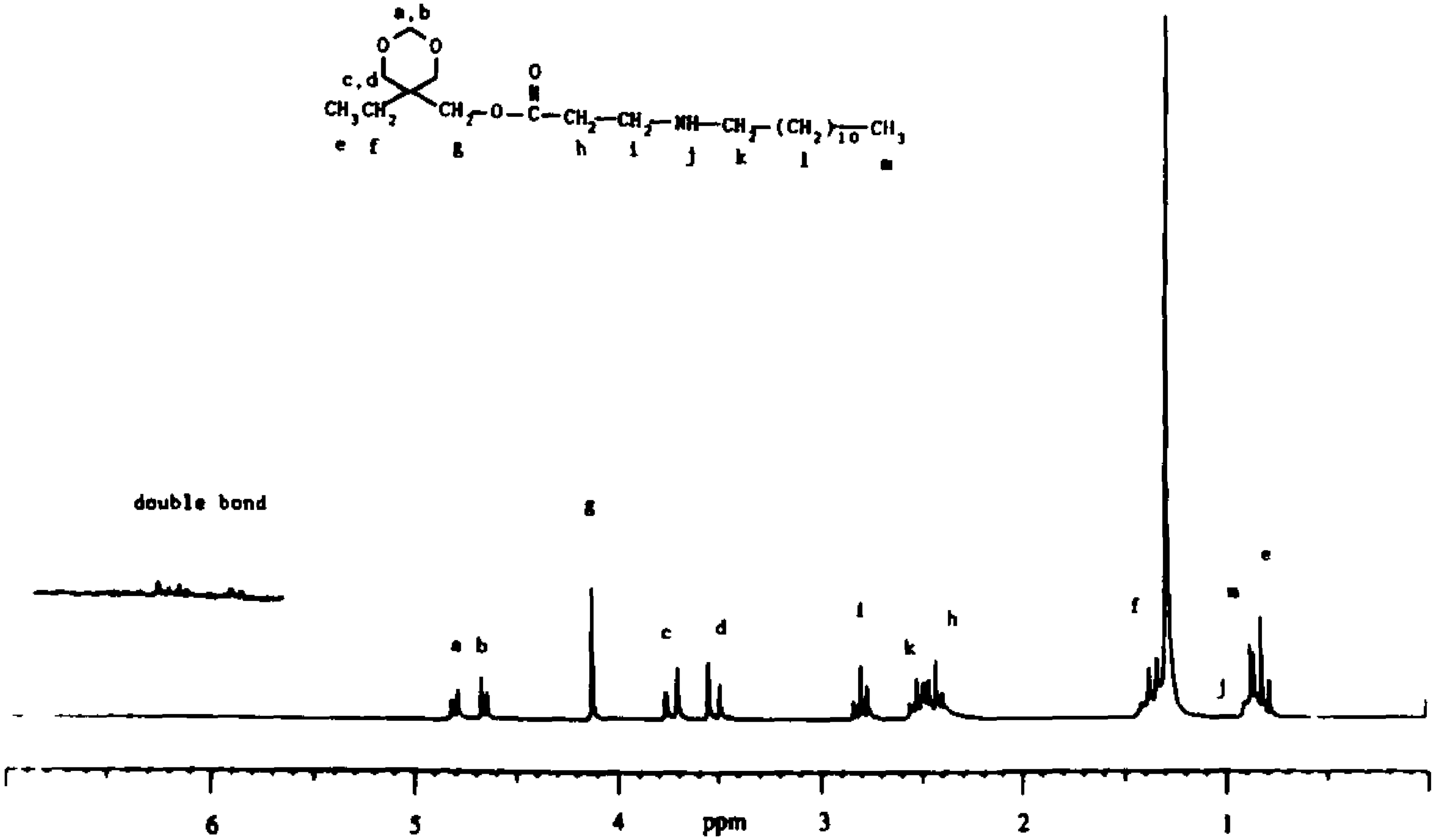


Fig. 2-13 ^{1}H NMR spectrum of comonomer 5-ethyl-5-methylacrylate-1,3-dioxane reacted with dodecylamine in DMSO-d_6 120 °C.

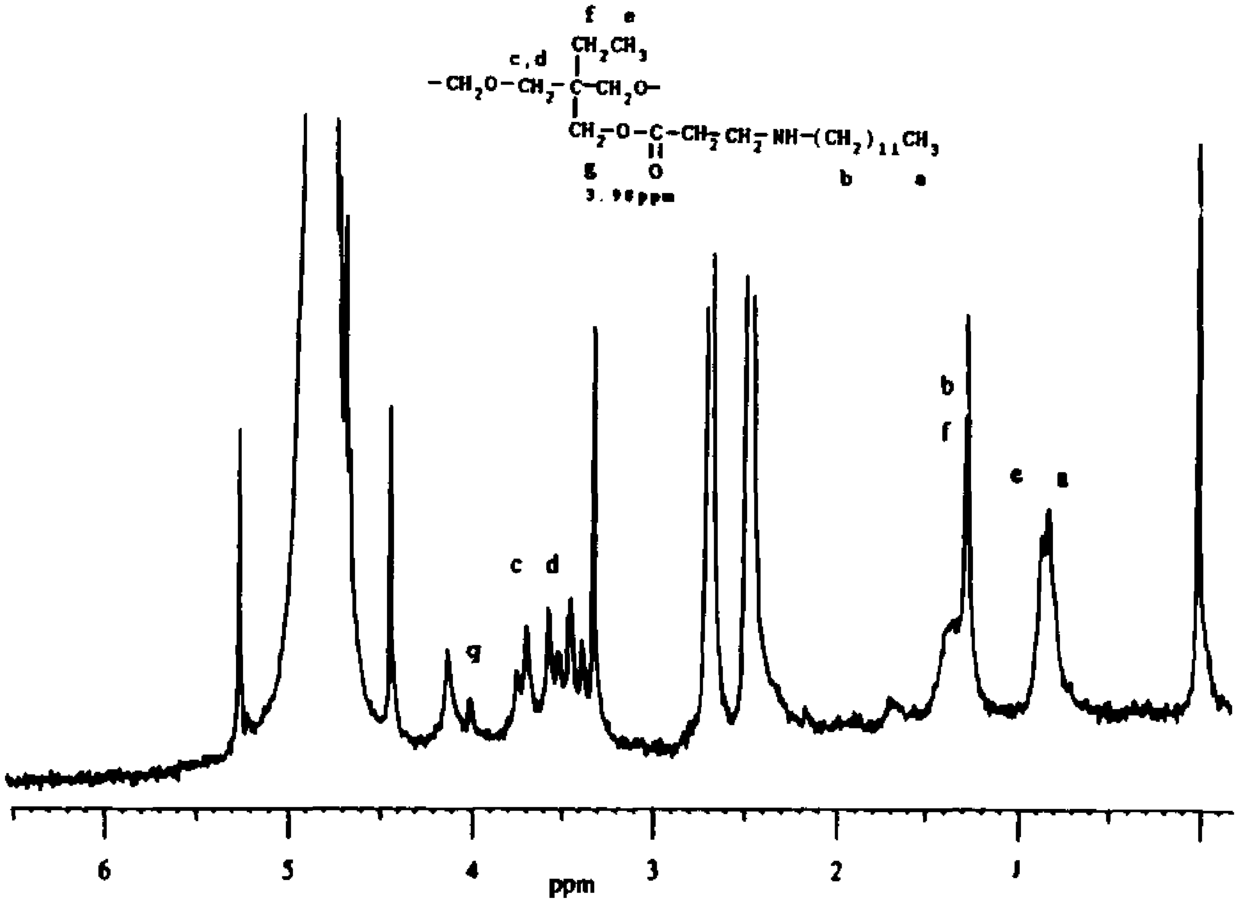


Fig. 2-14 ^1H NMR spectrum of copolymer of trioxane with 5-ethyl-5-methylacrylate-1,3-dioxane reacted with dodecylamine in DMSO-d_6 120 °C.

from 4.08 ppm to 3.98 ppm. The protons **h** and **i** are overshadowed by the strong absorptions of water (at 2.8 ppm) and solvent DMSO-d_6 (at 2.47 ppm). The peaks at 1.2-1.4 ppm are due to the methylene group from dodecylamine.

The reaction of the copolymer with polyamide is expected to be less efficient due to steric factors involving reactions of two large molecular species in a high viscosity medium and low concentration of amino end groups. The polyamide used is a terpolymer of nylon 6, 6-6 and 6-12 at equal proportion. The molecular weight is about 25 x 10^3. The carboxyl end groups were capped with the phenethylamine before used. Fig. 2-15 shows a ^{1}H NMR spectrum of the polyamide. The ^{1}H NMR spectrum of copolymer TOX with EMADO reacted with the polyamide at 170 °C for 2 hours is shown on Fig. 2-16. The peak at 1.2-1.6 ppm due to methylene group $-(CH_2)_4-$ from polyamide can be used to calculate the grafted polyamide, 13% by weight of polyamide was found in this sample.

For an efficient graft process, the copolymer should have high double bond content and not give off formaldehyde during the reaction. It should not have homopolymer of trioxane, or unstable end groups. Crosslink of the copolymer should be minimized. As the feed of EMADO increases for the copolymerization, the incorporation of EMADO and the double bond content increase. However, when the feed of EMADO is higher than 10% by mole, the incorporation does not increase further for bulk

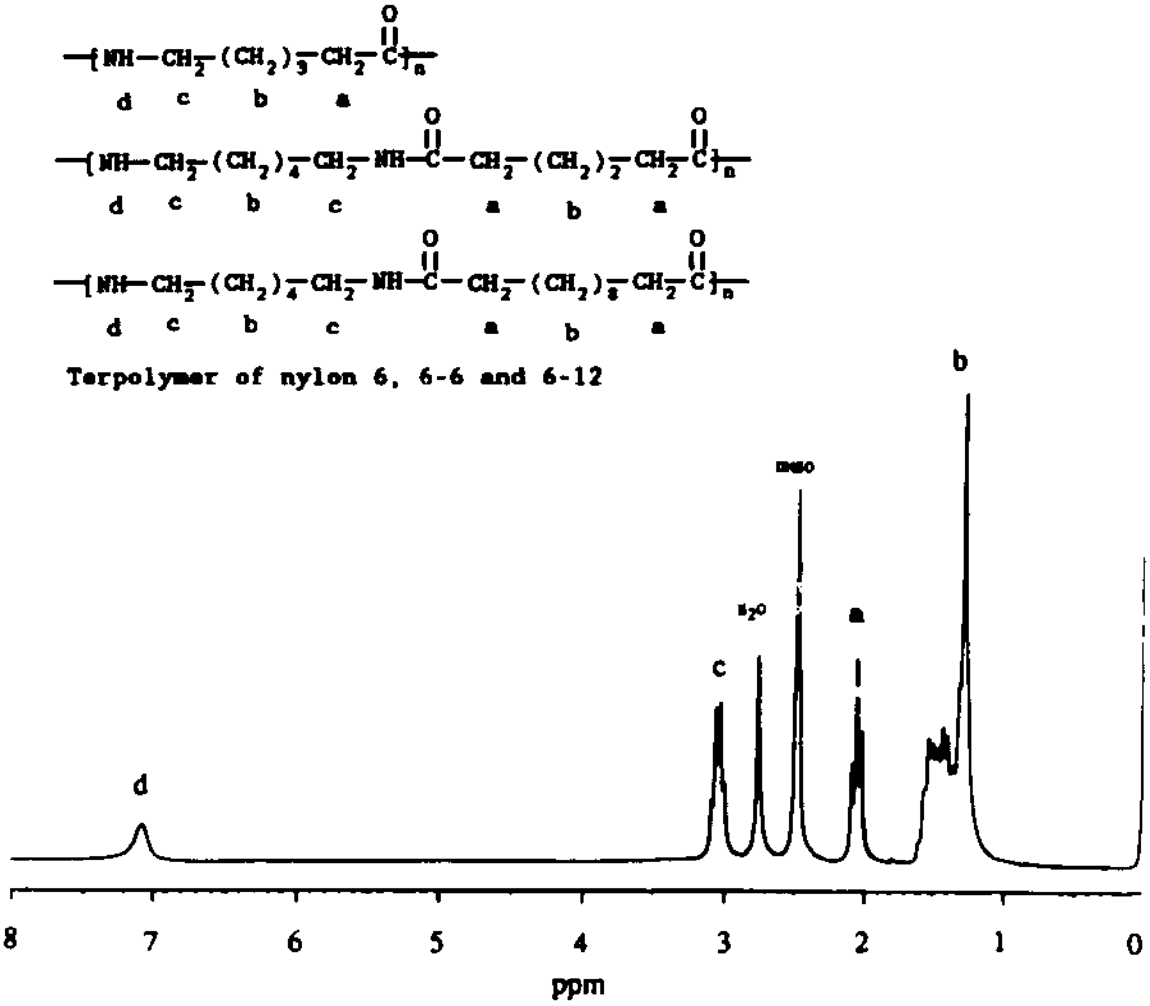


Fig. 2-15 ^1H NMR spectrum of polyamide in DMSO-d_6 at 120 °C.

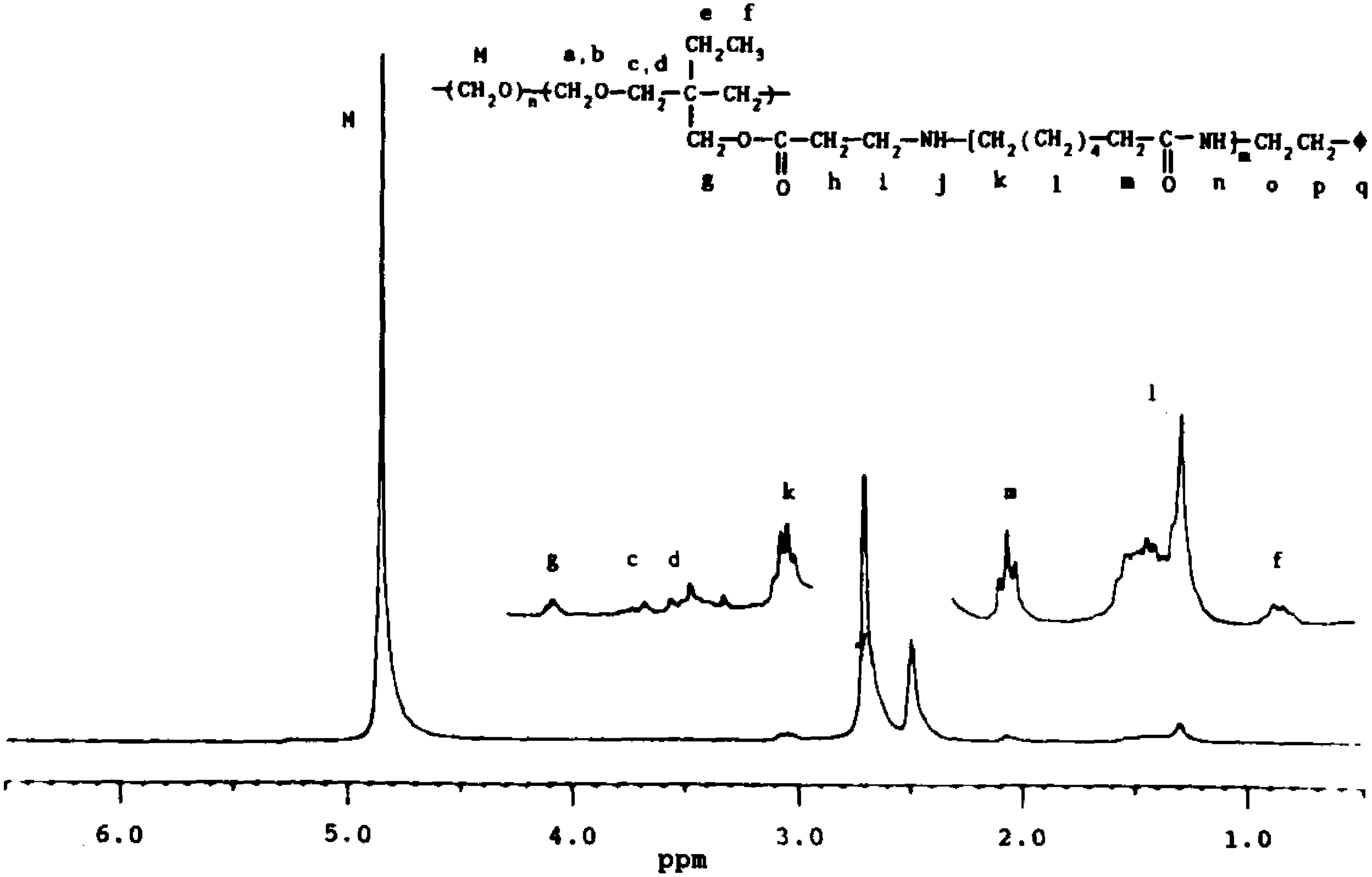


Fig. 2-16 ^1H NMR spectrum of copolymer of trioxane with 5-ethyl-5-methylacrylate-1,3-dioxane reacted with polyamide in DMSO-d_6 120 °C.

copolymerization. In general, the molecular weight of the copolymer decreases as comonomer EMADO feed increases. But molecular weight may also be affected by the content of initiator and water. For example, a copolymer prepared from trioxane with stringent control of water content and a low initiator amount had a high molecular weight of 6.4×10^4 (Table 2-2). Higher molecular weight leads, as expected, to higher tendency to crosslink.

When the incorporation of double bond is higher than 0.4 mole% the polyamide graft can reach 8-13% by weight (e.g. Fig. 2-16). Table 2-3 shows viscosity data for copolymers and grafted copolymers. The increase in molecular size is due to the graft. Since percent graft was only ca. 10% by weight, this increase in viscosity must be due to preferential interaction of graft side chain with hexafluoroisopropanol, the solvent for the measurement. For sample, E-60 is a mixture of sample Y-18 and polyamide with the same weight % as the polyamide portion in grafted polymer sample

Table 2-3 Molecular size of copolymers EMADO and graft copolymers

Sample number	Grafting Weight %	η_{inh}** dl/g	Calculated molecular weight
Y-18		0.60	17×10^3
EG-60	9.75	0.78	30×10^3
E-60*	9.75(mixture)	0.53	11×10^3
Y-19		0.66	21×10^3
EG-62	9.60	0.81	33×10^3

*E-60, mixture of sample Y-18 and polyaimde

** Concentration 0.200 g/dl

EG-60. The lower η_{inh} of the mixture E-60 than the grafted copolymer EG-60 indicates that the polyamide was indeed grafted in sample EG-60. Additional evidence of graft is from the precipitation temperature of copolymer from solution. Copolymer precipitated from DMSO at 108 °C, but the graft copolymer precipitated at 102°C. Both DMSO and HFIP are expected to have stronger solvation power for polyamide than for copolymers.

2.3.7. Thermal analysis of copolymers

For determination of heat of fusion and crystallinity of copolymer, accuracy of integrating the areas of endotherm is important. The DuPont Thermal Analysis 2100 system provides a DSC program with three baseline types: Linear, straight line from start to stop; Sigmoidal, horizontals from start and stop; Sigmoidal, tangents at start and stop. In this study, a baseline type of sigmoidal with tangents at start and stop was used, giving a good reproducibility of crystallinity.

Fig. 2-17 shows the typical DSC curves for copolymer of trioxane with 5-ethyl-5-methylacrylate-1,3-dioxane (EMADO) for the first run and the second run. There are two endotherms for the first run and one for the second run. The main endotherm for the first run was close to that of second run. However the crystallinity from the first run ranged from 69-81 %, the second run showed much lower crystallinity (55-70 %, Table 2-4). This indicated that crystallinity from solution crystallization on cooling from the base hydrolysis of nascent copolymer is 10-15 % higher than that from melt crystallization.

Table 2-4 Crystallinity of copolymers and graft copolymers

Sample No.	Incorp. mol%	Crystallinity (%)		Melting Point (°C)			Type of Polymer
		1st Run	2nd Run	1st Run		2nd Ru	
Y-05	0.36	72±1	60±1	/	164±1	167±1	Bulk
Y-03	0.86	77±1	63±1	163±1	168±1	167±1	
Y-12	0.91	71±2	63±1	162±1	168±1	169±1	
Y-08	0.97	69±2	61±1	163±1	167±2	167±2	
Y-15	0.66	71±2	55±2	/	165±1	169±1	
Y-18	1.19	78±1	57±1	160±1	167±1	167±1	
Y-17	1.12	77±2	62±2	161±1	164±1	167±1	
2-123	2.75	81±1	70±1	164±1	167±1	170±2	Solution
2-131	2.73	80±1	69±1	161±1	169±1	169±1	
2-137	2.56	81±1	68±2	163±1	168±1	169±1	
EG-62	9.60*	69±2	49±1	159±1	165±1	165±1	Graft
EG-60	9.75*	68±2	50±1	162±2	167±1	166±2	

* Weight percent of graft

TGA thermograms of copolymers EHMDO and EMADO, homopolymer of trioxane, and copolymer of trioxane with ethylene oxide (Fig. 2-18) clearly show that the two comonomer units with reactive functional group serve also as efficient stable end group as well as unzipping stopper.

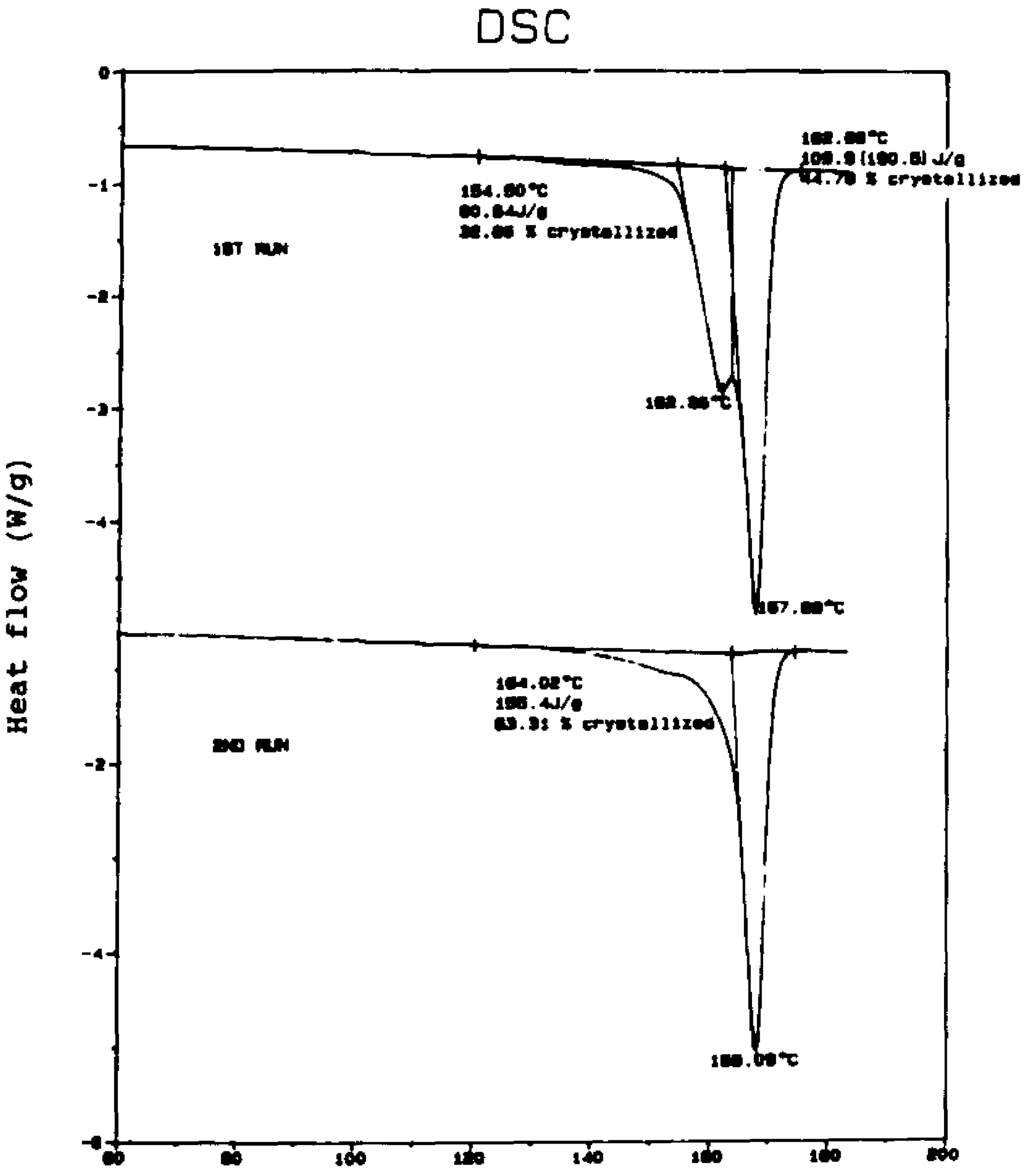


Fig. 2-17 Typical DSC curves for copolymer of trioxane with 5-ethyl-5-methylacrylate-1,3-dioxane for the first run and the second run.

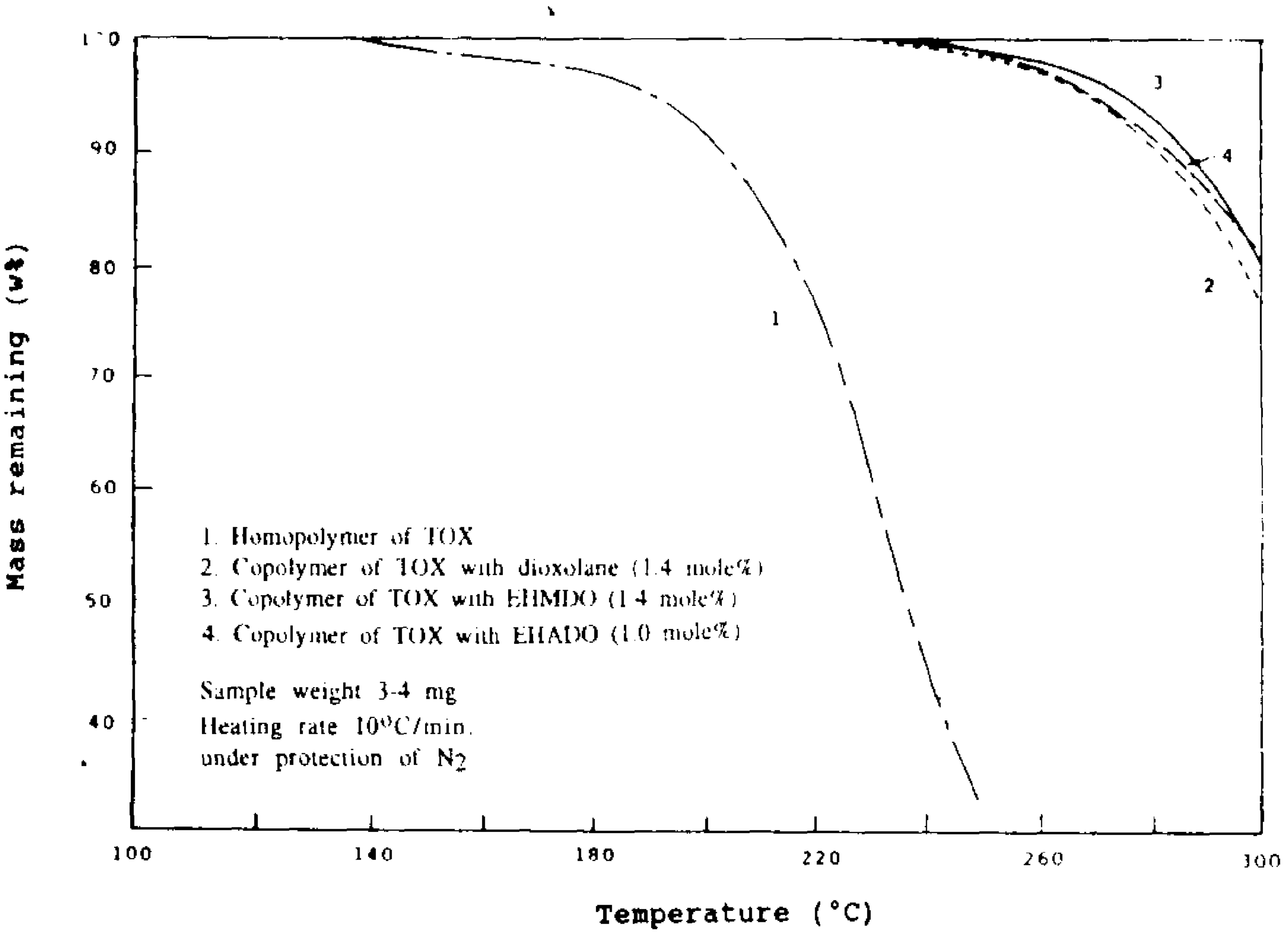


Fig. 2-18 TGA thermograms of copolymers.

2.4. Conclusion

Copolymerization of trioxane with 5-ethyl-5-hydroxymethyl-1,3-dioxane yields after base hydrolysis thermally stable low molecular weight copolymers with hydroxyl functional groups, which are reactive toward acylchlorides as well as isocyanates.

Copolymerization of trioxane with 5-ethyl-5-methylacrylate-1,3-dioxane yields after base hydrolysis thermally stable functionalized acetal copolymers with M_n in the range of 17 to 64 x 10^3. The level of double bond surviving the base hydrolysis ranges from 17 to 60 %. The crystallinity of the copolymers is ca. 55-70% from melt crystallization for molar incorporation at 0.5 to 1.0 mole% level based on CH_2O unit. The Michael addition reaction of the functionalized acetal copolymer was demonstrated through the formation of grafts with a polyamide.

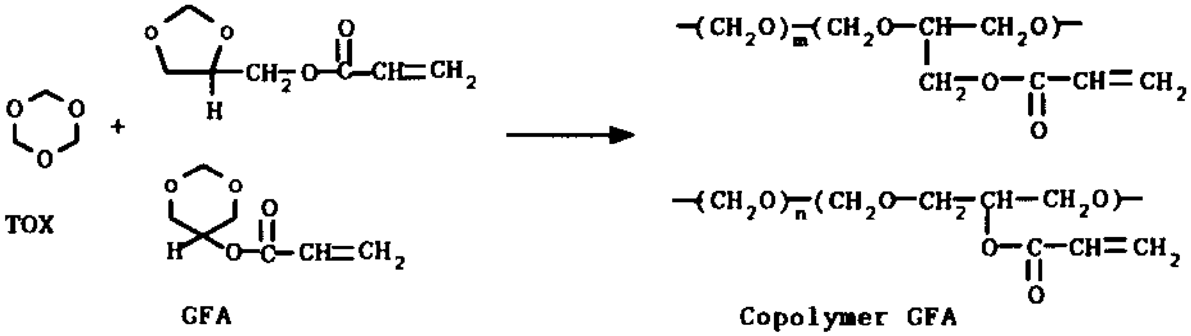
3. Copolymers of Trioxane with Glycerol Formal Derivatives

3.1. Introduction

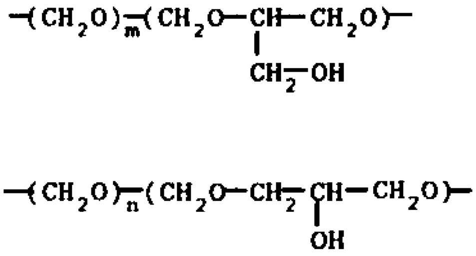
Glycerol formal consists of two cyclic acetal isomers, 1,3-dioxolane-4-methanol (α,β-isomer) and 1,3-dioxan-5-ol (α,α′-isomer), formed by the condensation of glycerin with formaldehyde[1]. The isomers can not be separated by either distillation or recrystallization. Quantitative ^1H NMR using a shift reagent, $Eu(fod)_3$[2], has been used to demonstrate that the isomeric composition is approximately 57% dioxane and 43% dioxolane at room temperature. The separation and determination of two isomers was accomplished by using high performance liquid chromatography[3]. Commercially available glycerol formals, e.g. from Aldrich Chemical Company, Inc., are an isomeric mixture at equilibrium. A mechanism was proposed to explain the equilibrium resulting from the presence of hydrogen ion[4], but no experimental evidence was available. In this study, separation and equilibrium of glycerol formal isomers are studied.

The cationic copolymerization of trioxane with glycerol formal was reported. A low molecular weight copolymer was obtained[4] due to the hydroxyl group of the formal.

The copolymerization of trioxane with the isomeric mixture of glycerol formal acrylate, GFA, gives copolymer GFA with acrylate functional groups.



In addition, glycerol formal benzoate (GFB) can be copolymerized with trioxane to obtain a copolymer GFB with pendant benzoate groups. The benzoate ester groups can be hydrolyzed giving a copolymer GF with pendant hydroxyl groups.



$$-(CH_2O)_m-(CH_2O-\underset{\displaystyle CH_2-OH}{\underset{|}{CH}}-CH_2O)-$$

$$-(CH_2O)_n-(CH_2O-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2O)-$$

Copolymer GF

Both pendant acrylate and hydroxyl groups can be reactive sites for further modification.

3.2. Experimental

3.2.1. Synthesis of glycerol formal benzoate (GFB) and separation of its isomers

Glycerol formal benzoate was synthesized through the reaction of glycerol formal with benzoyl chloride. Glycerol formal (52.0 g, 0.5 mole), triethylamine (76.5 ml, 0.55 mole) and toluene (50 ml) were placed in a 250 ml three neck flask fitted with a dropping funnel and a drying tube. A toluene (50 ml) solution of benzoyl chloride (77.3 g, 0.55 mole) in the dropping funnel was added dropwise under stirring over a period of 30 minutes into the glycerol formal solution kept at a cold water bath. The reaction mixture, a suspension, was stirred at room temperature for 10-12 hrs. The solid by-product $Et_3N{\cdot}HCl$ was filtered off from the reaction mixture. The filtrate was washed twice with water (2x50 ml) and separated. After removing toluene using a rotary evaporator under vacuum, a purified product (94.0 g) was obtained by distillation of the crude product at reduced pressure (b.p. 133-138 °C/2-3 mm; Yield 72.7 %).

The α,α-isomer of glycerol formal benzoates (1,3-dioxan- 5-benzoate) can be crystallized at 0°C from the mixture and separated by filtration. The crystals were washed with carbon tetrachloride and dried. The filtrate contains about 20% of α,α' form and 80% of α,β form of glycerol formal benzoate.

3.2.2. Preparation of isomers of glycerol formal, α,β and α,α′-isomers

The α,α′-isomer of GFB, 1,3-dioxane-5-benzoate, was hydrolyzed using KOH solution to give α,α′-isomer of GF, 1,3-dioxan-5-ol. 1,3-dioxane-5-benzoate (20.8 g, 0.10 mol), KOH (6.3 g, 0.11 mol) and distilled water (20 ml) were added to a 100 ml round bottom flask. The reaction mixture was heated at 100°C for about 30 min. until the mixture become a clear homogeneous solution. The water in the solution was then removed using a rotary evaporator at 60°C under reduced pressure. A white solid remained in the flask. 1,3-Dioxan-5-ol in the solid was extracted by ether 3 times (3x20 ml), then the ether was evaporated and 1,3-dioxan-5-ol was collected. The yield was 50 %.

The α,β-isomer of GFB can be hydrolyzed into α,β-isomer of GF using a similar method. The α,β-isomer of GF thus obtained contains about 20 % of α,α′ form.

3.2.3. Equilibrium of isomers of glycerol formal (GF)

In a 5 mm NMR tube, 0.4 ml of DMSO-d_6 and 4 μl of 1,3-dioxan-5-ol were added. The tube was heated to 120 °C in the NMR probe for initial observation. 4 μl of D_2SO_4 was then added to the tube and the ^1H NMR spectra were recorded every 5 minutes until the system reached equilibrium.

3.2.4. Syntheses of glycerol formal acrylate (GFA) and glycerol formal acetate (GFAc)

Glycerol formal acrylate and glycerol formal acetate were synthesized through a similar procedure used in preparing glycerol formal benzoate mentioned in section 3.2.1.

3.2.5. Syntheses of copolymers of trioxane with glycerol formal acrylate (copolymer GFA), glycerol formal benzoate (copolymer GFB) and glycerol formal acetate (copolymer GFAc)

The copolymerization of trioxane with comonomers was carried out in bulk using a procedure similar to those described in section 2.2.3.

A dry test tube (25x150mm) with a magnetic stirrer was charged with 9 grams of trioxane. The tube was then capped with a serum stopper, purged with nitrogen and evacuated through a needle connecting the serum stopper to a vacuum pump. The desired amount of comonomers was injected into the tube through the serum stopper. The contents of tube were kept in an oil bath at 65°C. Then the required amount of boron trifluoride etherate was injected through the serum stopper into the completely melted mixture under stirring. After addition of the initiator, the colorless mixture become a milky white solid within a few minutes. The polymerization was allowed to proceed at 65°C for 20 hrs. At the conclusion of the polymerization, the polymer was removed and pulverized in a blender. The crude polymer was then stirred in 30 ml of methanol containing 1% of triethanolamine, TEA, for 1 hr and then collected by filtration and dry. The typical yield was about 85%.

All copolymers were hydrolyzed under basic conditions to eliminate unstable end groups as described in section 2.2.4.

3.2.6. Preparation of copolymer of trioxane with glycerol formal (copolymer GF)

Copolymer of trioxane with glycerol formal can be prepared through the hydrolysis of the ester group of copolymer GFB or copolymer GFA. The procedure is as follows: 7.9 g of copolymer GFB and 79 ml of 2N NaOH aqueous solution were placed in a 250 ml round bottom flask equipped with a magnetic stirrer and a condenser. The copolymer was suspended in the aqueous solution at 100 °C for ca. 12 hrs. At the conclusion of the reaction, the mixture was filtered, washed with water until the filtrate was neutral, then washed again with acetone three times and dried under vacuum at 45°C. Under such conditions, the ester groups for copolymers GFA and GFB was completely hydrolyzed.

3.2.7. Graft of copolymer GFA

Dodecylamine, a low molecular weight liquid amine, can be removed from the reaction mixture after graft reaction by washing with acetone. An example of the procedure used for graft reaction is as follow: 0.20 g of copolymer GFA containing 2.85 mole % of double bond, 0.20 g of dodecylamine and 3.0 ml of DMSO as solvent were placed in a 10 ml of round bottom flask equipped with a magnetic stirrer and a condenser. The content was kept at 165-170 °C for 0.5 hrs under stirring. After cooling the reaction mixture, the grafted copolymer was precipitated then filtered and washed 3 times with acetone to remove the unreacted amine. Finally the copolymer was dried under vacuum at 40 - 50 °C overnight. 0.16 g of graft copolymer was obtained.

3.2.8. Graft of copolymer GF

Copolymer GF, carrying the hydroxyl groups can be grafted with phenylisocyanate. The grafting procedure was as follows: 0.2 g of copolymer GF, 0.2 g of phenylisocyanate and 1.5 ml N,N-dimethylacetamide were placed in a 10 ml round bottom flask equipped with a magnetic stirrer and a condenser. The reaction was carried out at 160 °C for 2 hrs. Then the reaction mixture was cooled to precipitate the copolymer. The copolymer was washed with acetone 3 times to remove unreacted phenylisocyanate. The final product was dried and then subject to NMR determination.

A similar procedure was used for graft reaction of copolymer GF with octadecyl isocyanate.

3.2.9. NMR characterisation of comonomers and copolymers

All NMR spectra were obtained on an IBM 200-SY NMR spectrometer operated at 200 MHz for proton using Bruker software. The chemical shifts were referenced to tetramethylsilane at 0 ppm for ^1H spectra and DMSO-d_6 at 39.5 ppm for ^{13}C spectra.

The distortionless enhanced polarization transfer (DEPT) ^{13}C spectra were performed to identify the CH and CH_2 groups using a DEPT program from Bruker software. The 90° pulse width for solvent DMSO-d_6 was determined as 16.0 μs for ^1H and 15.0 μs for ^{13}C.

The homonuclear 2D correlated (COSY) spectrum of comonomer GFA was obtained using a standard pulse sequence RD-90°-t_1-90°-detect. The relaxation delay used is 1.0 s. The initial data matrix was 512 Hz in each dimension. The 2D data set was zero filled in both direction prior to Fourier transformation. A sine-bell filtering function was used in both dimension prior to Fourier transformation in order to improve the resolution.

3.2.10. Determination of molecular weight of copolymers

The molecular weight of the copolymer was estimated from inherent viscosity of the hexafluouroisopropanol (HFIP) solution of the copolymer with a concentration of 0.2 g/dl at 25°C. The inherent viscosity for the copolymers was compared to those of ethylene oxide-trioxane copolymer with 1.4 mole % incorporated with a large range of molecular weights. The molecular weight of copolymers was also estimated from the polymer end group analysis from NMR data, assuming one -OCH_3 end group per chain. All mole % of incorporation are based on formaldehyde as a comonomer unit.

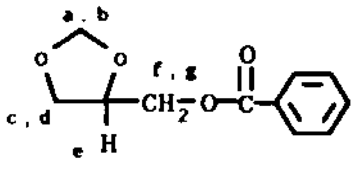
3.2.11. Thermal analysis of copolymers, thermal stability and crystallinity

The thermal stability and crystallinity of copolymer were determined by TGA and DSC techniques with a Model 2100 DuPont Thermal Analyzer, as described in section 2.2.9.

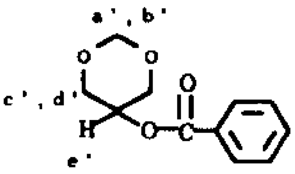
3.3 Results and Discussion

3.3.1. Synthesis of glycerol formal benzoate (GFB) and separation of its isomers.

The two isomers of glycerol formal benzoate (GFB) can be separated by crystallization[1].



α, β-isomer



α, α'-isomer

The α,α′-isomers, GFB(α,α′), can be crystallized at about 0°C from the isomeric mixture. The α,β-isomers, GFB(α,β), remains as a liquid. The GFB(α,α′) crystal was removed by filtration and washed with CCl_4 or cyclohexane three times. Fig. 3-1 shows a ^1H NMR spectrum of GFB(α,α′) in DMSO-d_6 at 120°C. The protons, **a′** and **b′** are not equivalent and form an AB system, exhibiting a doublet at 4.80 ppm and a second doublet at 4.96 ppm. The protons, **c′** and **d′**, coupled with proton **e′**, form an ABX system, giving two doublets (3.98 and 4.12 ppm) with each absorption further splitted into a doublet of equal intensity due to coupling with **e′**. The proton **e′** shows a multiplet at 4.90 ppm. The absorption peaks in the region 7.5 to 8.0 ppm are due to the phenyl group.

Fig. 3-2 shows a ^1H NMR spectrum of the mixture of an isomers of GFB used in polymerization. The ratio of two isomers remains the same in the original glycerol formal.

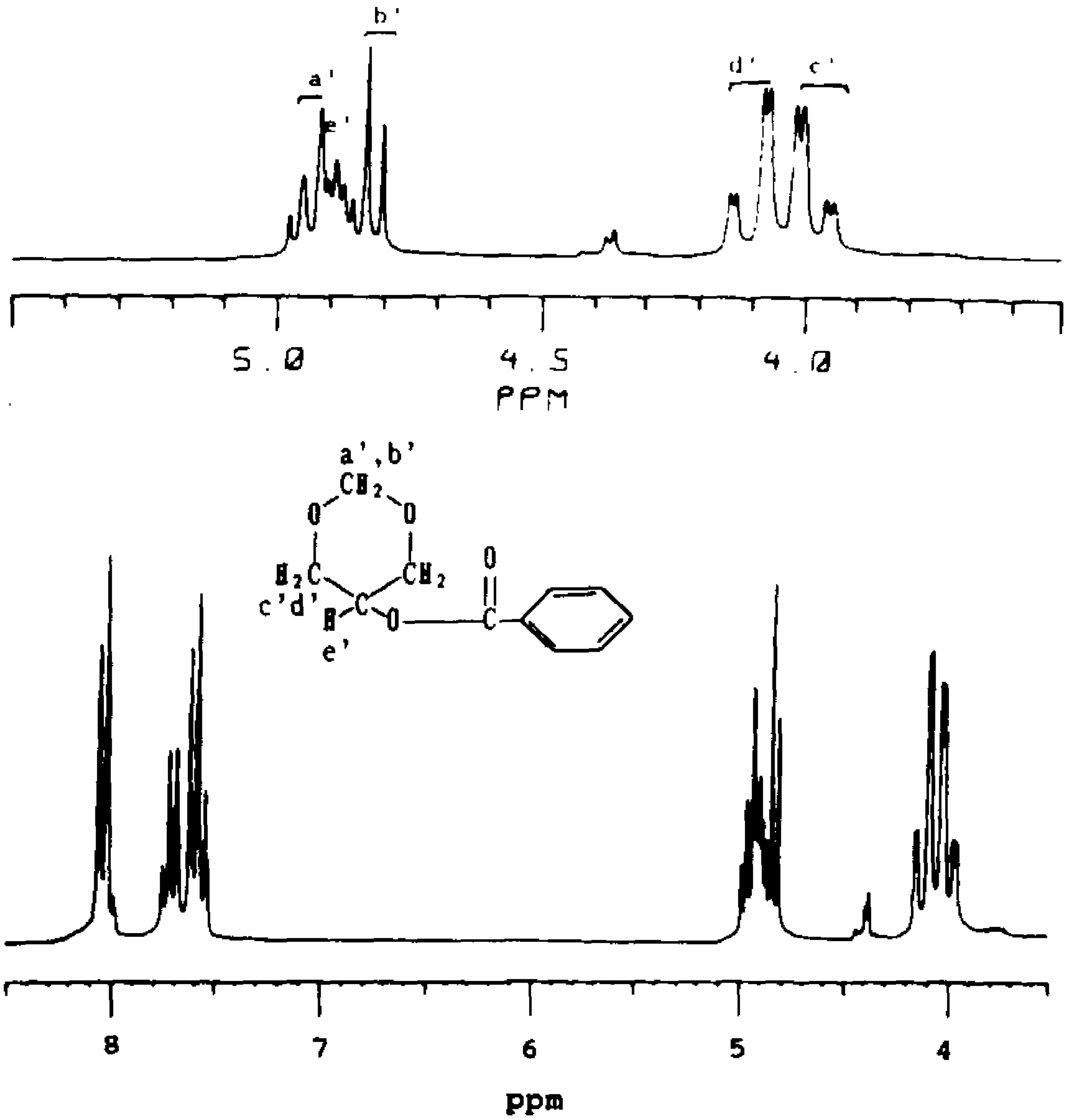


Fig. 3-1 ^{1}H NMR spectrum of α,α′-isomer of glycerol formal benzoate in DMSO-d_6 at 120 °C.

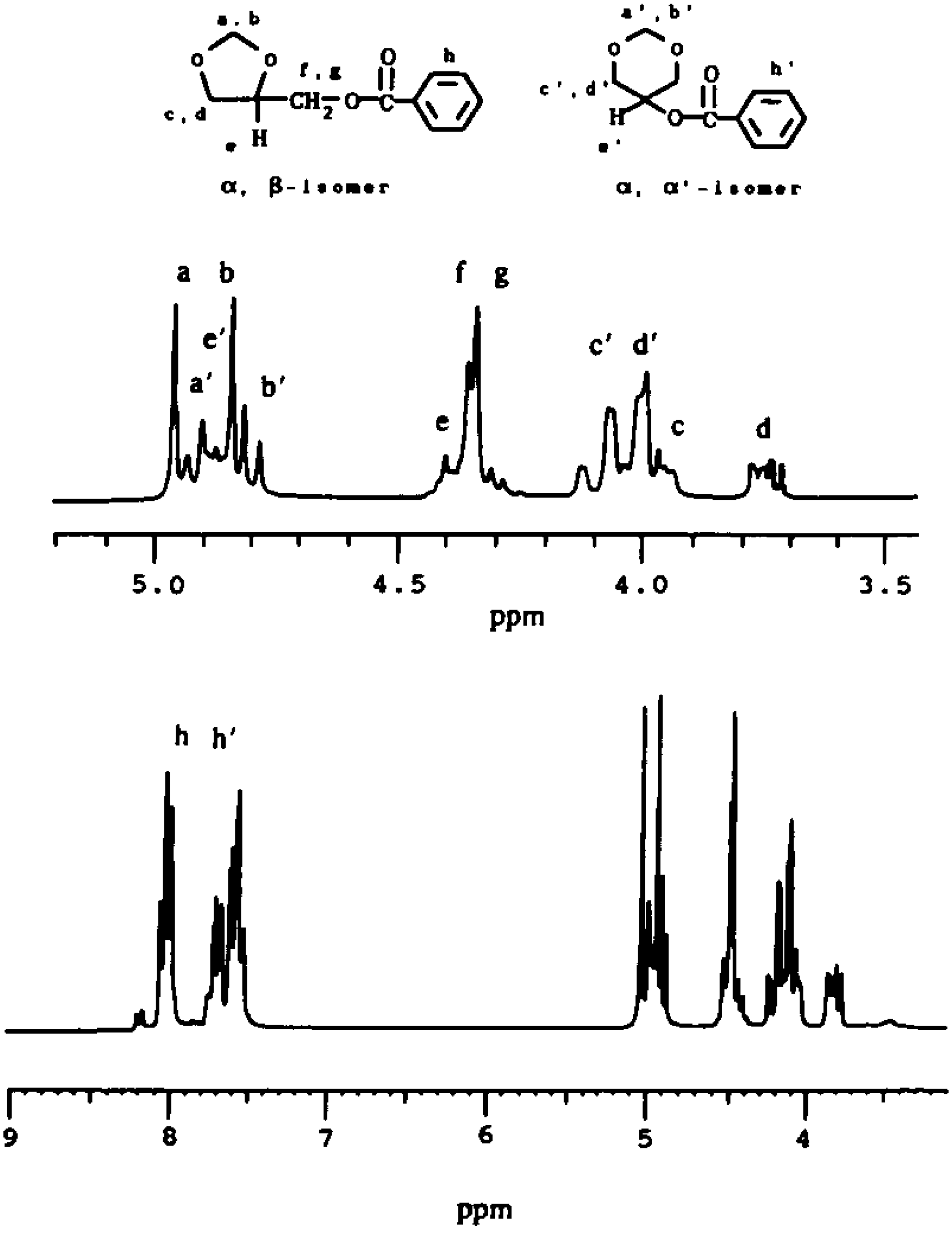


Fig. 3-2 ^{1}H NMR spectrum of glycerol formal benzoate in DMSO-d_6 at room temperature.

3.3.2. ^{1}H NMR of isomers of glycerol formal, α,β and α,α′-isomers

Fig. 3-3 shows a ^{1}H NMR spectrum of α,isomer of glycerol formal in DMSO-d_6 at room temperature. An AB-quartet pattern was seen with the two doublet centered at chemical shifts of 4.51 and 4.76 ppm. They are assigned to protons **a′** and **b′** in 2-position in its ring. The multiplet at 3.46-4.10 ppm is assigned to proton **e′** of the methine group. There are two quartets at 3.25-3.38 ppm and 3.85-3.96 ppm due to proton **c′** and **d′** in the 4- and 6-positions. Other weak absorption are due to protons from the α,β-isomer.

Fig. 3-4 (a) shows a ^{1}H NMR spectrum of α,β-isomer (with small amount of α,α′-isomers) in DMSO-d_6 at 120 °C. Two singlets at 4.77 and 4.88 ppm are due to the protons **a** and **b** in 2- position. A multiplet at 3.95-4.05 ppm is due to the proton **e** in the methine group. Another multiplet at 3.95-4.05 ppm is due to two protons, **f** and **g**, connected with the hydroxyl group. The other protons, **c** and **d**, are assigned at 3.55-3.64 ppm (quartet) and 3.80-3.90 ppm (quartet). Addition small peaks are due to protons from the α,α′-isomer.

The isomeric ratio of glycerol formals can be determined directly in chloroform-d (Fig. 3-5). The singlet at 5.03 ppm (1 proton **a′** of α,β-isomer) and a half quartet of an AB system at 4.72 ppm (1 proton **b** of α,α′-isomer) is used to calculate the ratio of α,β-isomer and α,α′-isomer

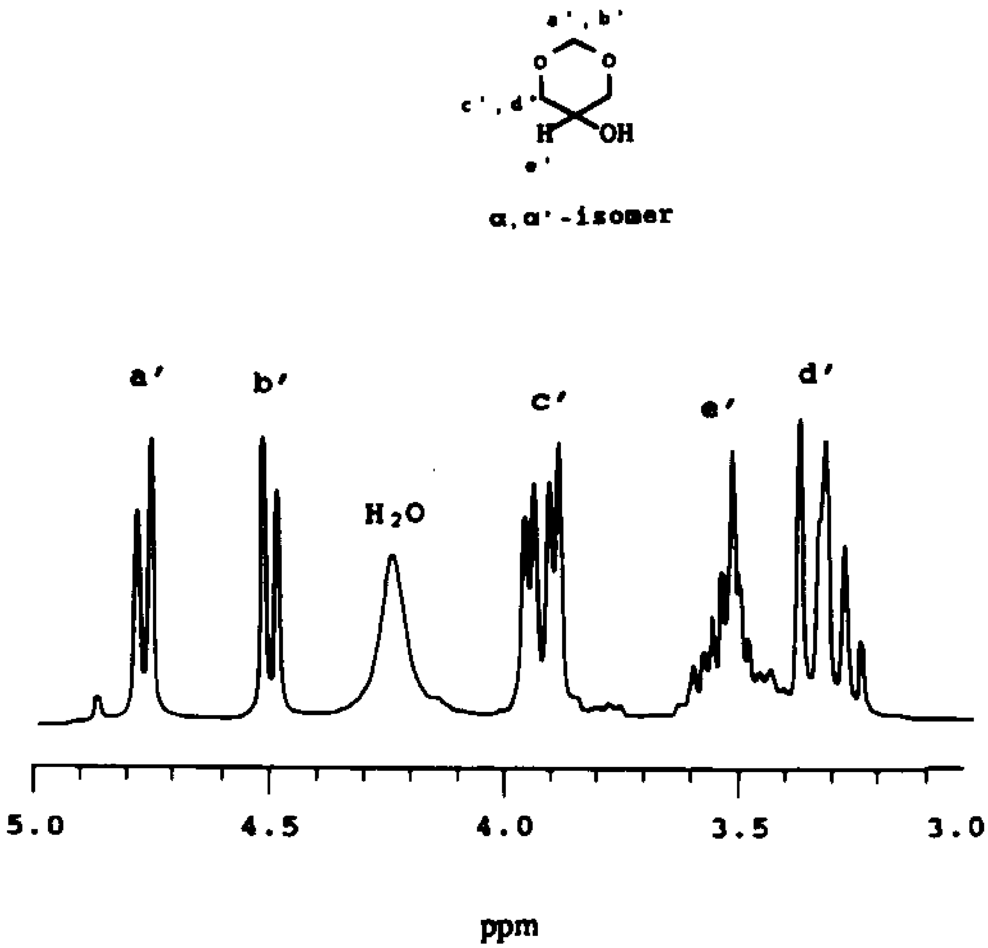


Fig. 3-3 ^1H NMR spectrum of α,α'-isomer of glycerol formal in DMSO-d_6 at room temperature.

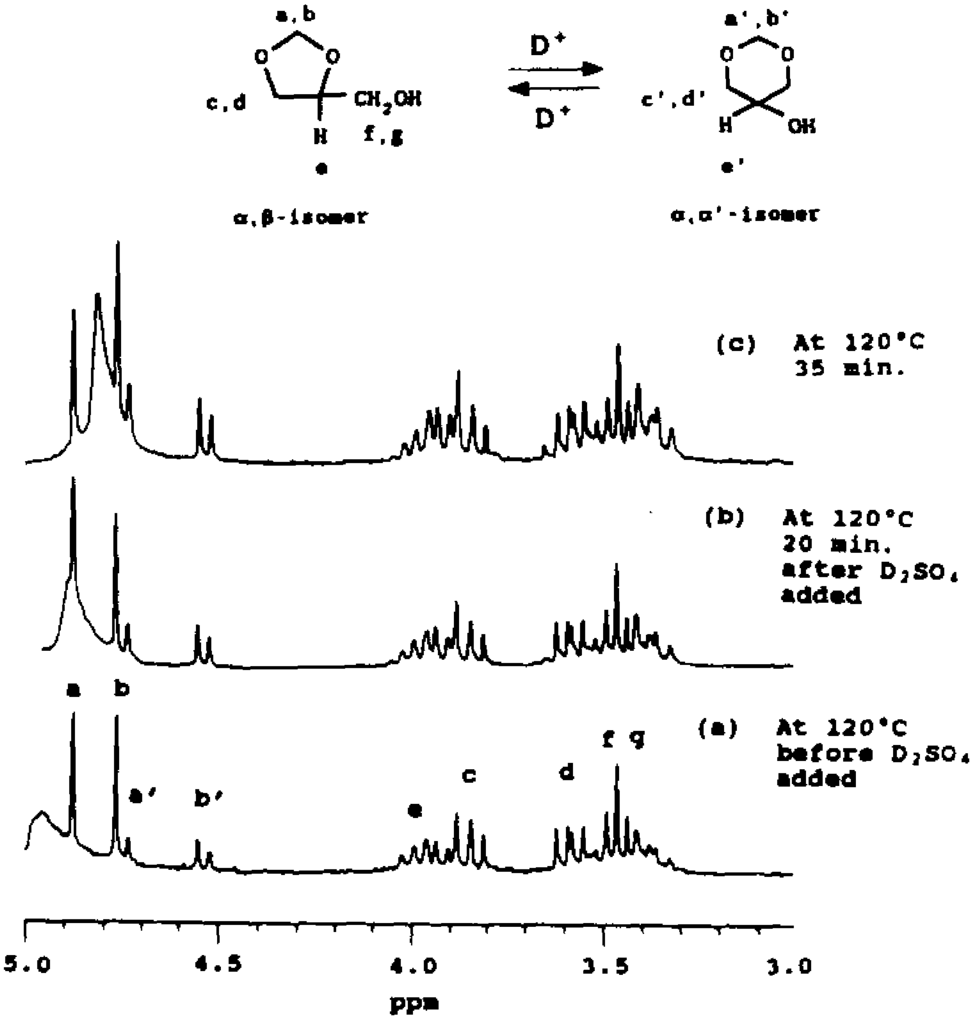


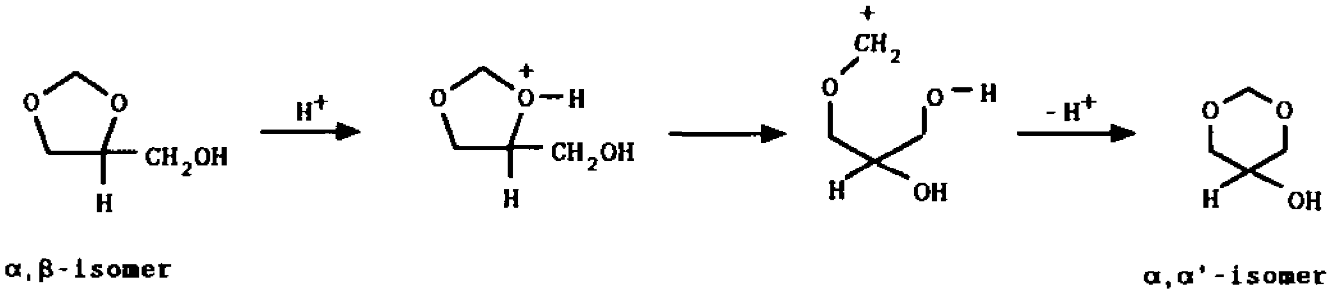
Fig. 3-4 ^1H NMR spectrum of α,β-isomer of glycerol formal in DMSO-d_6 at 120 °C.

without having to resort to the use chemical shift reagent[2]. A sample of glycerol formal from Aldrich Chemical Company, Inc. was analyzed. The ratio of dioxolane and dioxane was 43/57, the same value as determined with the use of shift reagent.

^{13}C NMR data confirm results from ^{1}H NMR. Fig. 3-6 (b) shown a ^{13}C NMR spectrum and assignment of glycerol formal with ~80 mole% of α,β-isomer and 20 mole% of α, α′-isomer. A ^{13}C NMR spectrum of α,α′-isomers shown in Fig. 3-6 (a) is used for the assignment of spectrum (b).

3.3.3. Equilibrium of glycerol formal (GF) isomers

The two isomers of glycerol formal are at equilibrium with the concentration ratio of isomers depending on temperature. A mechanism to reach the equilibrium was proposed as follows[4]:



The presence of H^+ is required for the process of equilibrium. A sample of α,β-isomer (or α,α′-isomer) obtained from hydrolysis of glycerol formal benzoate was shown to be stable from room temperature to 120°C, no change

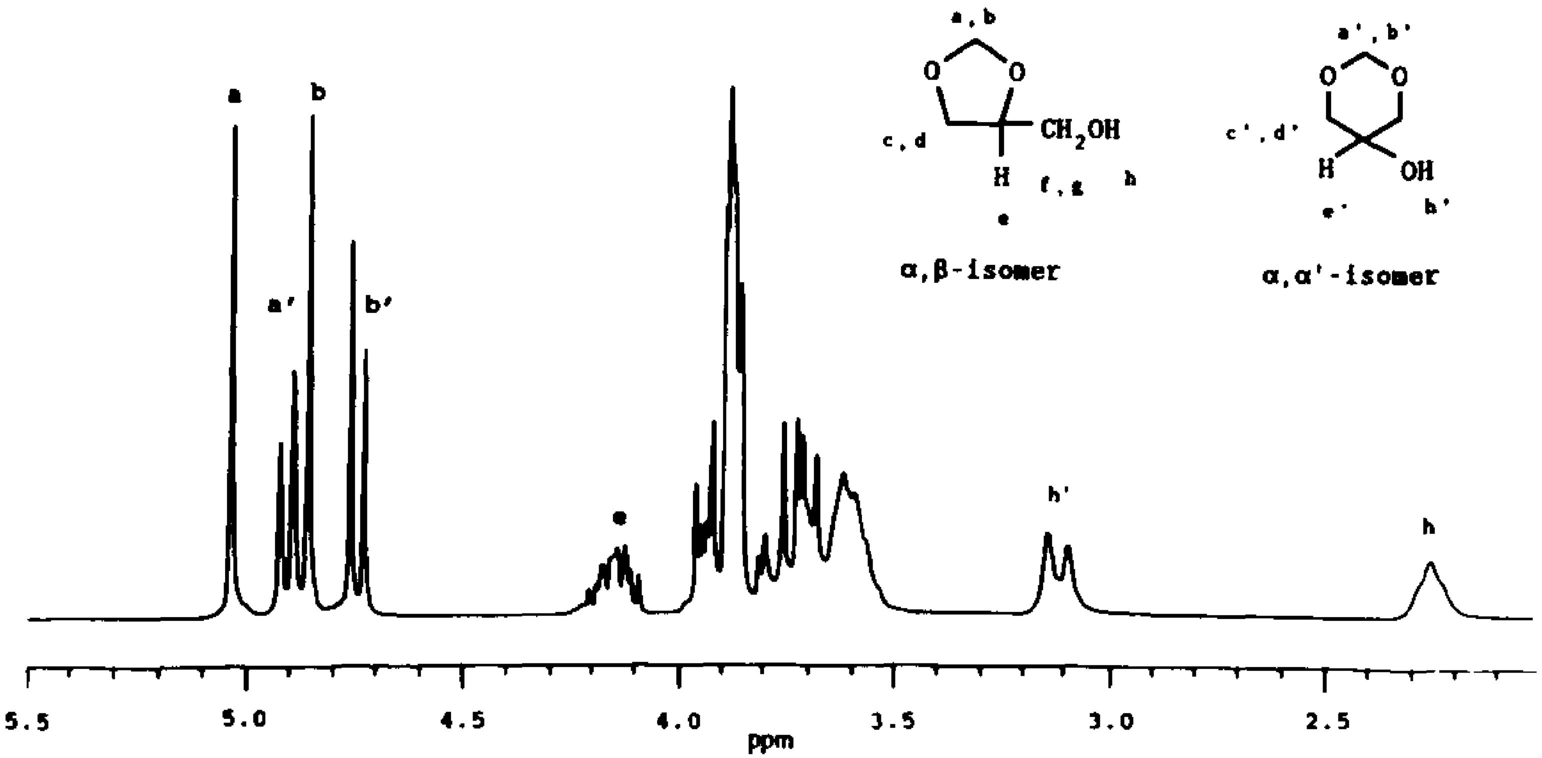


Fig. 3-5 ^{1}H NMR spectrum of glycerol formal in chloroform-d at room temperature.

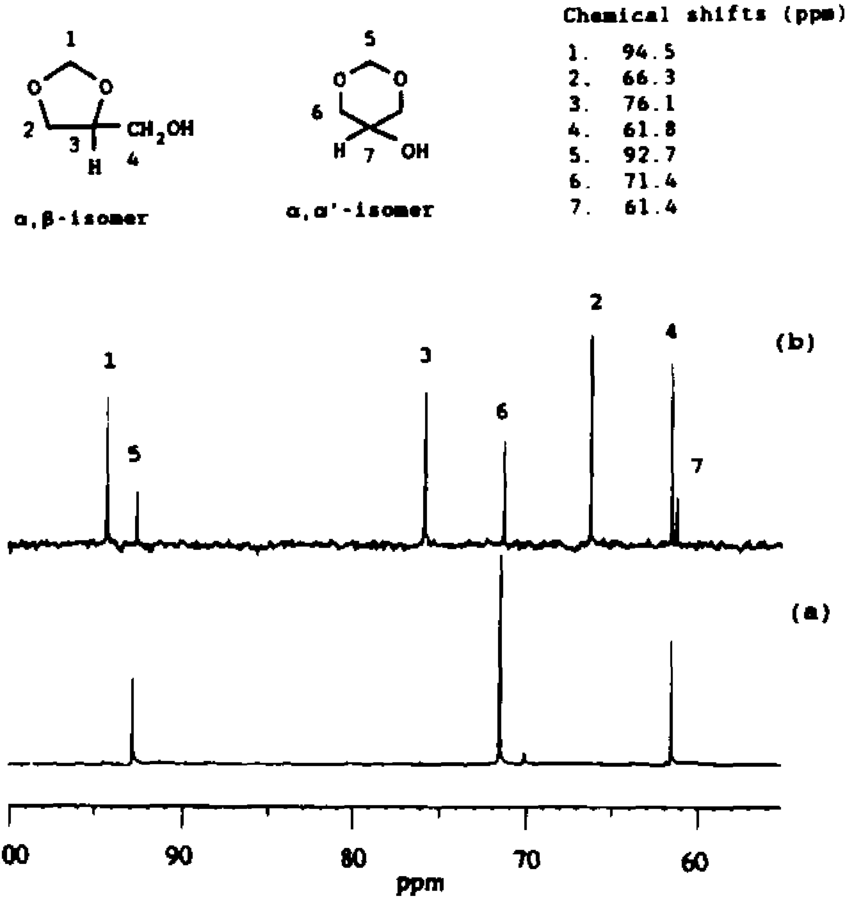


Fig. 3-6 (a) ^{13}C NMR spectrum of α,α'-isomer of glycerol formal at 120°C;

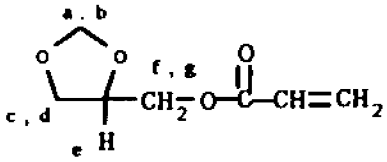
(b) ^{13}C NMR spectrum of glycerol formal with 20% of α,β-isomer and 80% of α,α'-isomer DMSO-d_6 at 120°C.

in isomeric ratio was observed. Thus, H^+ is required for the isomerization to reach equilibrium.

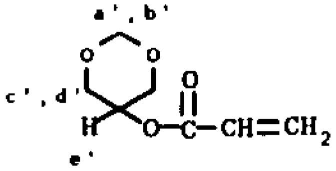
Fig. 3-7 is a serial of ^1H NMR spectra of α,α'-isomer in DMSO-d_6 with added D_2SO_4 at 120°C. Starting with 3 mole % of α,β-isomer, after 35 minutes of adding D_2SO_4 the mole % of α,β-isomer increase to 47.2 mole % and then remains at the same equilibrium ratio. A similar experiment starting with the other isomer, α,β-isomer (Fig. 3-4 b and c) leads to the same ratio.

3.3.4. Structure determination of glycerol formal acrylate (GFA) and glycerol formal acetate (GFAc)

^1H NMR spectra of the GFA isomeric mixture at RT and 120°C are shown in the Fig. 3-8. The two isomers, like GF, can not be separated by distillation or crystallization. The ^1H NMR spectrum of the mixture is rather complex. The complete ^1H NMR assignments shown in the figure are based on data from the study of the α,α'-isomer of glycerol formal benzoate.



α,β-isomer



α,α'-isomer

Since GFA(α,α') has a structure similar to GFB(α,α'), its ^1H NMR assignment at 120°C (Fig. 3-8 A) can be readily established: **a'** and **b'**, singlet at 4.81 ppm; **e'**, multiplet

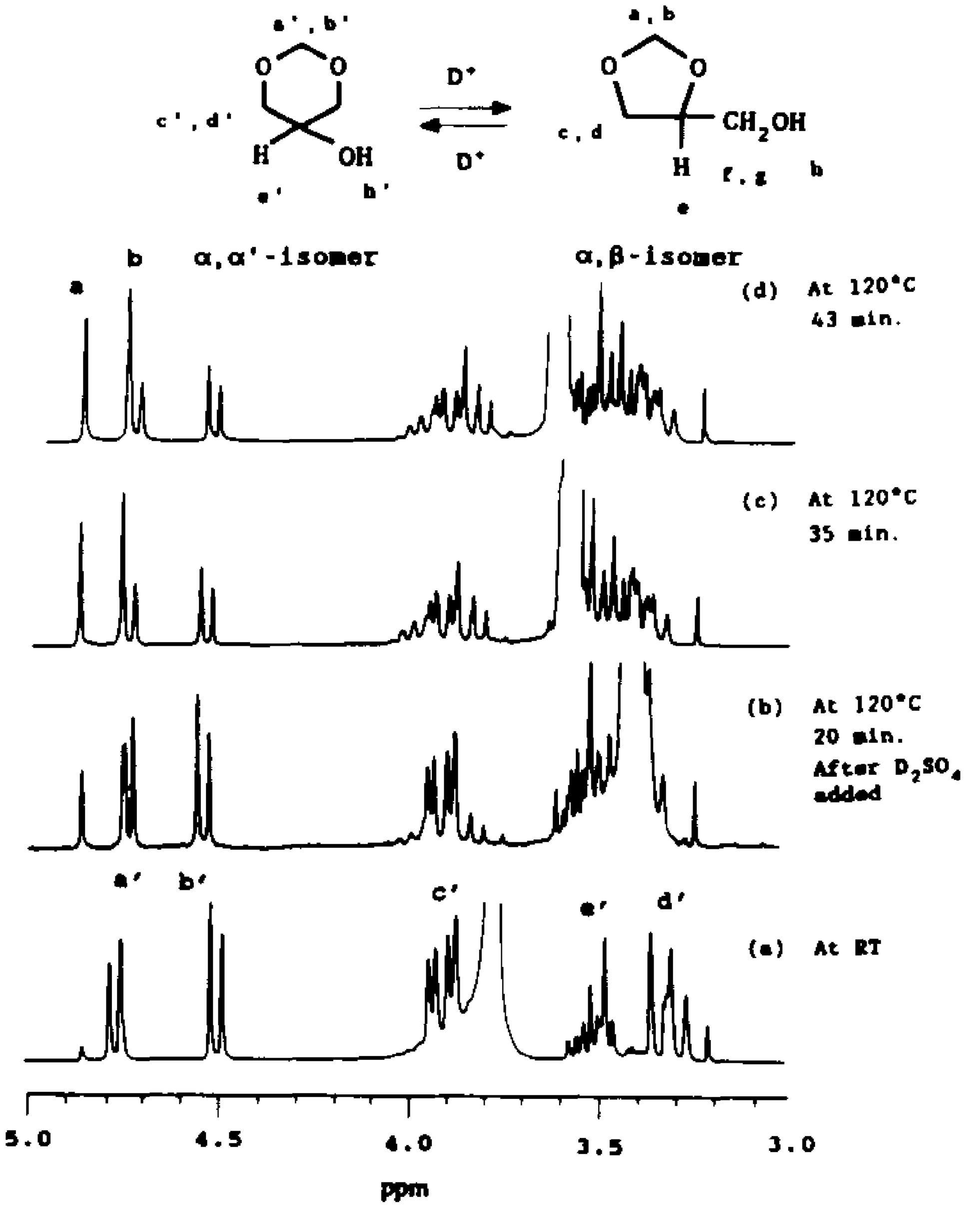


Fig. 3-7 ^{1}H NMR spectra of α,α′-isomer of glycerol formal in DMSO-d_6 with D_2SO_4 at 120 °C.

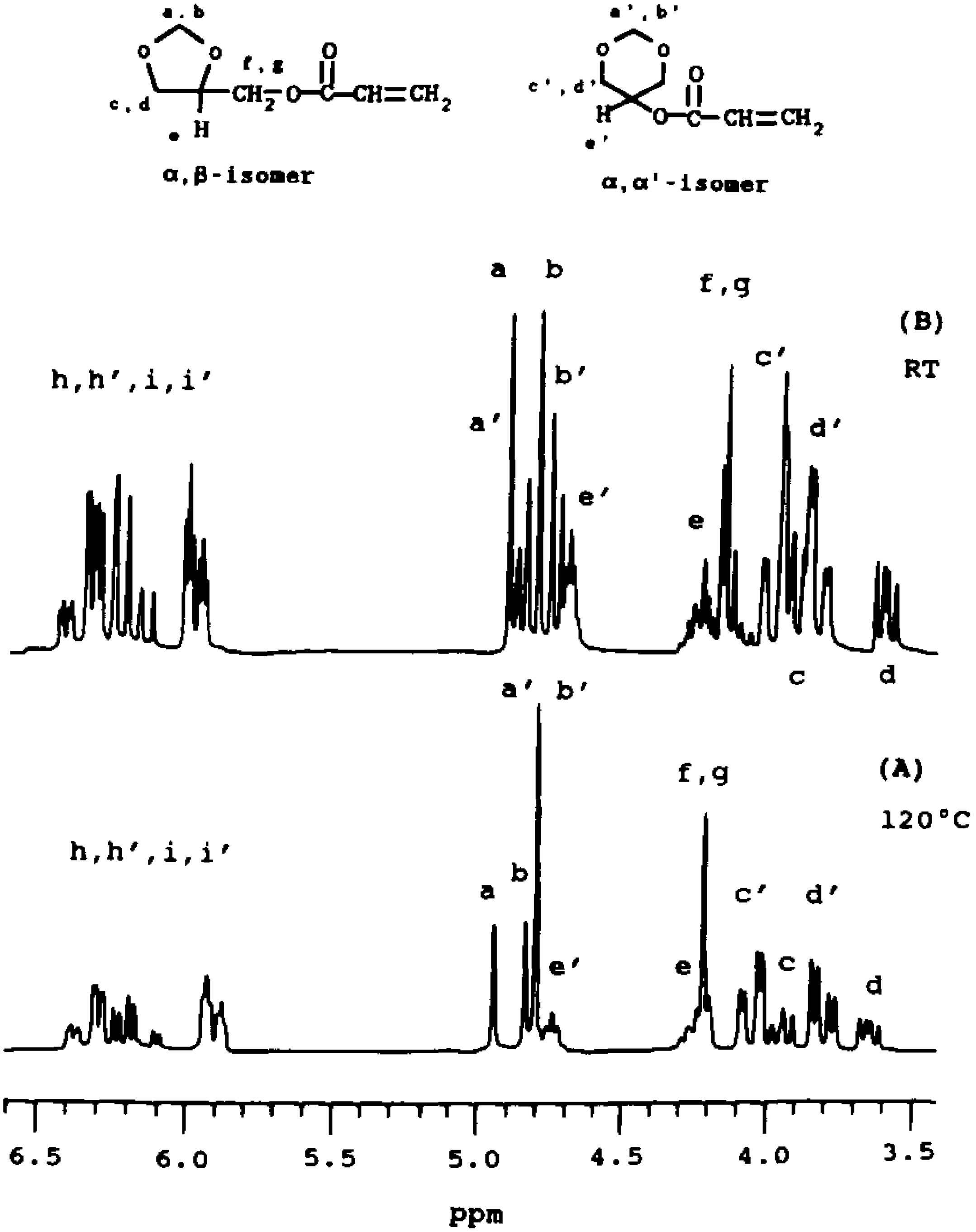


Fig. 3-8 ^{1}H NMR spectrum of glycerol formal acrylate in DMSO-d_6 at 120 °C (A) and room temperature (B).

at 4.74 ppm; **c'** and **d'**, doublets (coupled further with **e'** to give two doublets each) at 3.80 and 4.07 ppm. The assignments for the other isomer, GFA(α,β) are then forthcoming. Its protons **c** and **d** couple with **e** to form an AMX system, leading to absorptions at 4.25 ppm (multiplet) for **e**, 3.65 ppm (quartet) for **c** and 3.92 ppm (quartet) for **d**. The protons **f** and **g** also couple with **e** to form a complex system with absorptions at 4.20 ppm (multiplet). The protons **a** and **b** in the five-member ring system are not equivalent, resulting in two singlets at 4.82 and 4.93 ppm.

The assignments for ^{1}H NMR spectrum of GFA at room temperature (Fig. 3-8 B) are similar as at 120°C. The absorption of proton **a'** and **b'** at room temperature is an AB system with two doublets centered at 4.76 and 4.88 ppm, instead of a singlet at 4.81 ppm at 120°C. This is due to the rapid conformational change of the dioxane ring at this high temperature resulting in an equivalent magnetic environment for protons **a'** and **b'**.

The assignments given above for GFA were further ascertained through homonuclear decoupling experiment at room temperature. When proton **e'** is irradiated, protons **c'** and **d'**, no longer coupled with **e'**, become an AB system with two doublet absorptions (Fig. 3-9 c). Similarly, when **e** is irradiated, protons **c** and **d** become an AB system; protons **f** and **g** also become an AB system (Fig. 3-9 b).

Fig. 3-10 shows a portion of COSY 2D NMR spectrum of glycerol formal acrylate. It is apparent from the cross

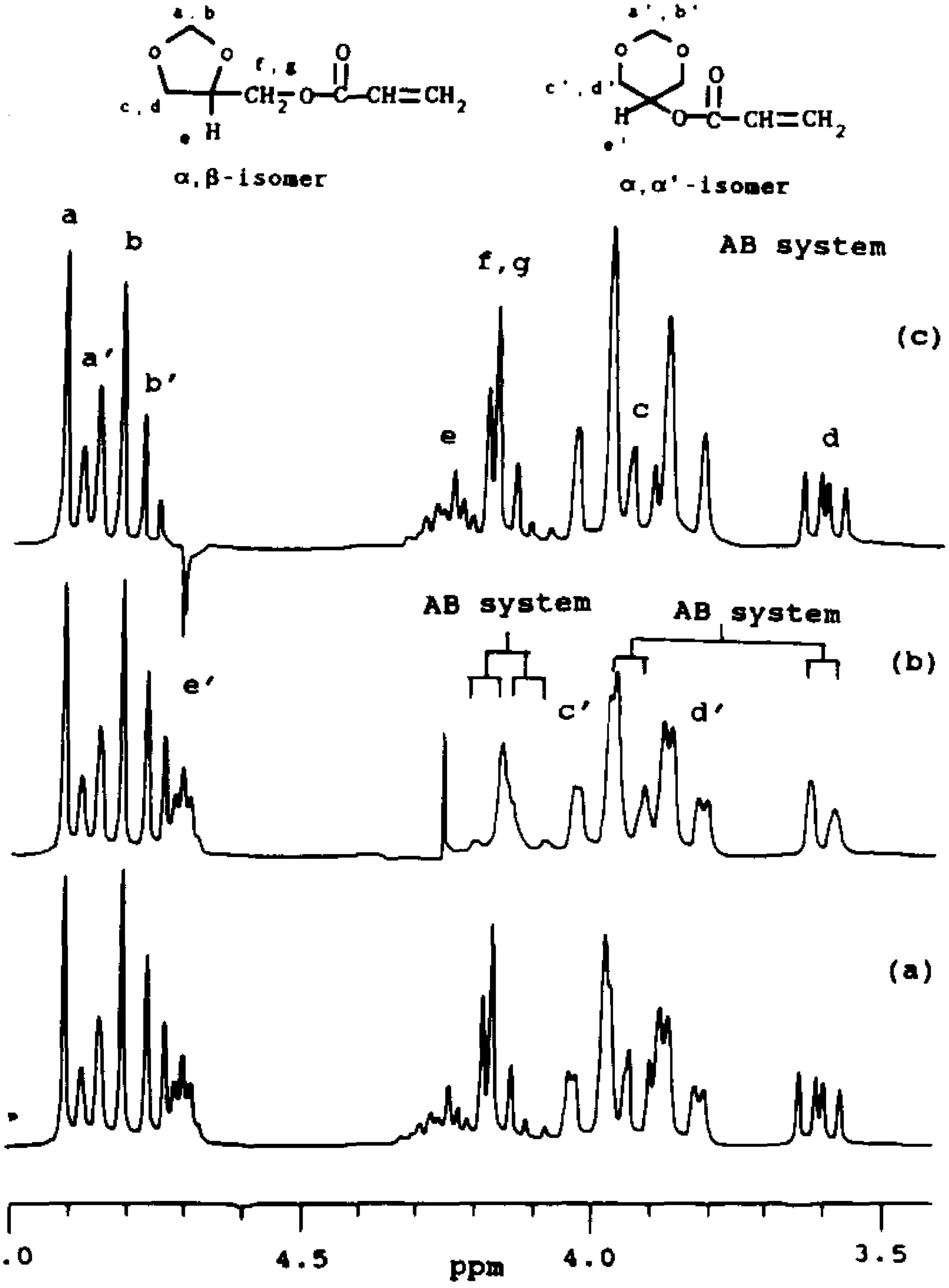


Fig. 3-9 Portion of homonuclear decoupling ^{1}H NMR spectrum of glycerol formal acrylate in DMSO-d_6 at 120 °C.
a. Original ^{1}H NMR spectrum;
b. Decoupling power focus on proton e;
c. Decoupling power focus on proton e'.

Fig. 3-10 Portion of COSY spectrum of glycerol formal acrylate in DMSO-d_6 at 120 °C.

peaks on the Figure that proton **e** coupled with protons **c** and **d**, **f** and g, while proton **e′** couple with protons **c′** and **d′**.

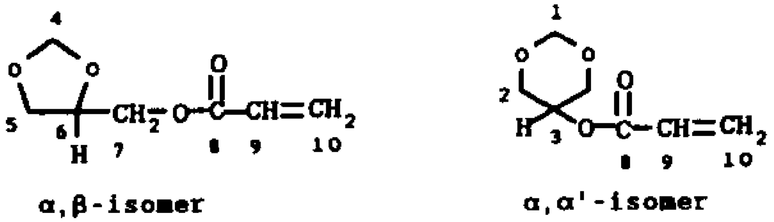
Fig. 3-11 (a) shows a ^{13}C NMR spectrum of the GFA isomers with its assignment, which are based on the ^{13}C NMR data from the isolated isomer GFB(α,α′) (Fig. 3-11(b)).

The GFB(α,α′) sample used still contains a small amount of its isomer GFB(α,β), which gives the weak absorptions in the spectrum. The assignment for all carbons can be readily made through peak intensity ratios as well as established chemical shifts for similar functionalities. The ^{13}C absorptions for GFA(α,α′) should be close to those for GFB(α,α′). A comparison of spectrum in (a) with spectrum in (b) leads to the complete assignments for GFA(α,β) and GFA(α,α′).

The mole % of the isomers in the mixture can be readily calculated from the integrated spectral intensities (Fig. 3-8), e.g.:

$$\begin{aligned}\begin{array}{l}\alpha,\alpha'\text{-Isomeric}\\ \text{content (mole\%)}\end{array} &= \frac{\alpha,\alpha'\text{-isomer}}{\alpha,\alpha'\text{-isomer} + \alpha,\beta\text{-isomer}}\\ &= \frac{\text{Peak }(a + b)}{\text{Peak }(a + b + a' + b')}\\ &= 56\text{-}57\%\end{aligned}$$

Fig. 3-12 shows a ^{1}H NMR spectrum of glycerol formal acetate in DMSO-d_6 at room temperature.



Chemical shifts (ppm)

1. 92.2
2. 67.1
3. 66.6
4. 94.1
5. 64.3
6. 65.6
7. 72.5
8. 164.2, 164.4
9. 127.5, 127.7
10. 129.5, 129.7

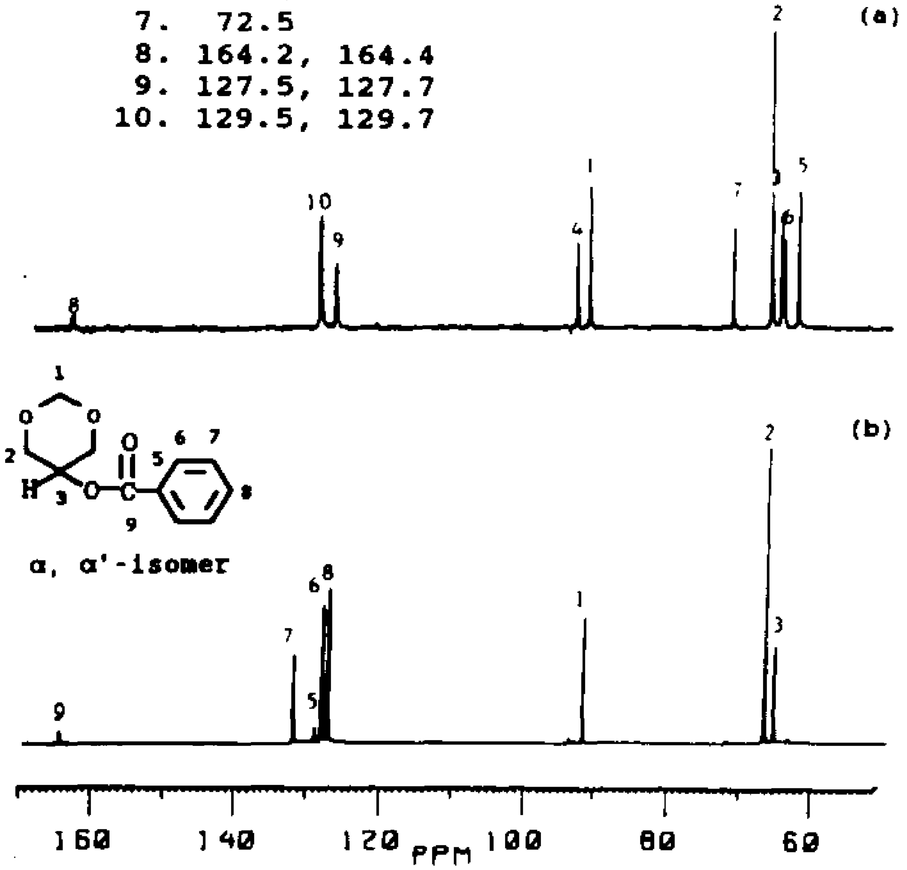


Fig. 3-11 ^{13}C NMR spectrum of glycerol formal acrylate (a) and α,α'-isomer of glycerol formal benzoate (b) in DMSO-d_6 at 120 °C.

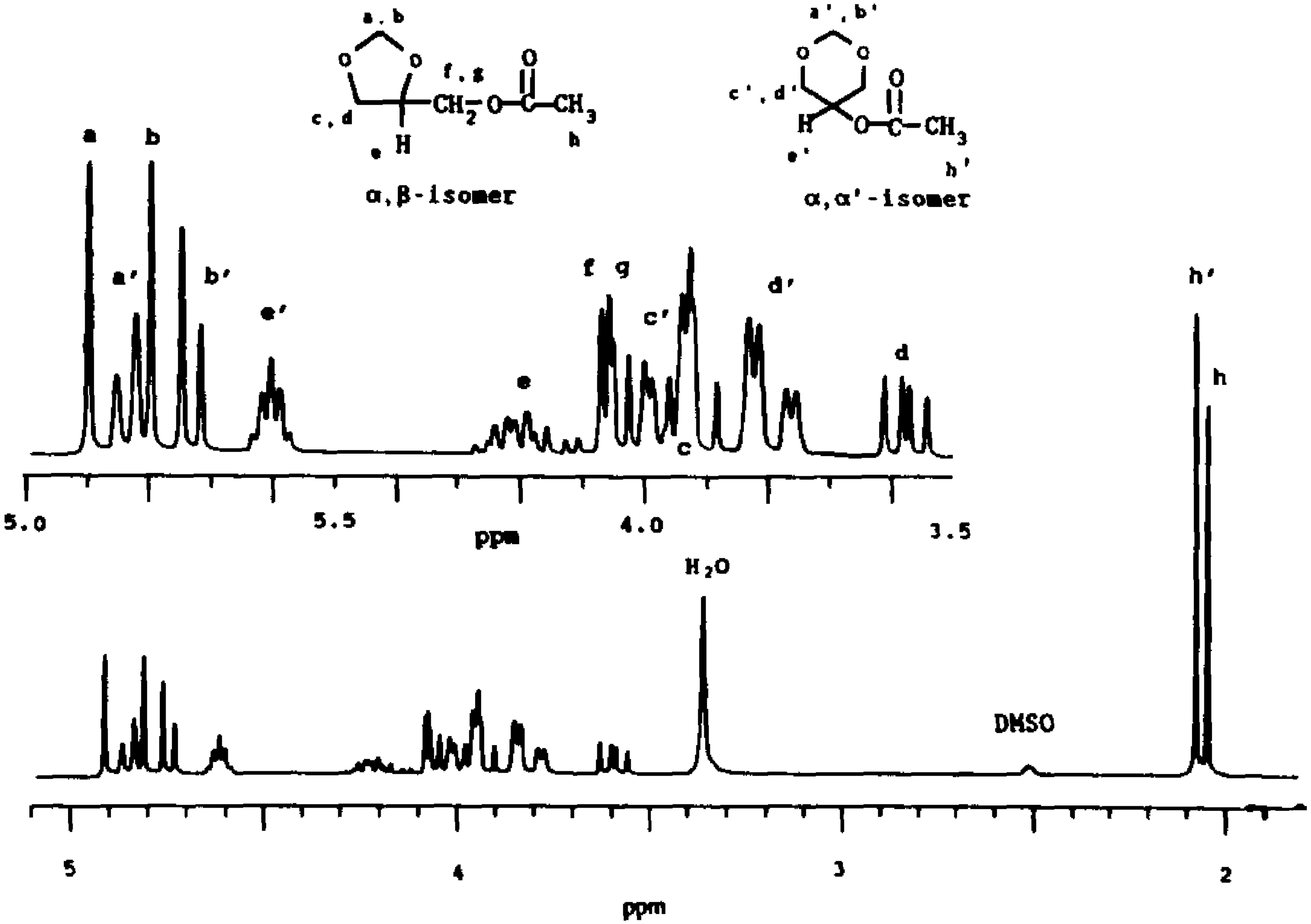
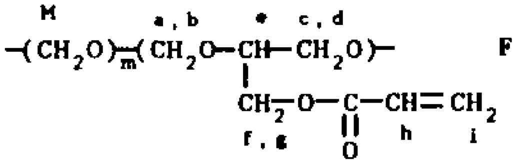


Fig. 3-12 ^{1}H NMR spectrum of glycerol formal acetate in DMSO-d_6 at room temperature.

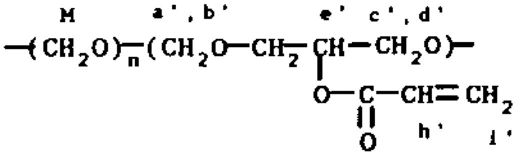
3.3.5. Copolymers of trioxane, (TOX), with glycerol formal acrylate, (GFA), glycerol formal benzoate, (GFB), and glycerol formal acetate, (GFAc)

(a) ^1H and ^{13}C NMR Assignment for copolymer GFA.

The copolymerization of TOX with the two GFA isomers leads to the following structural units:



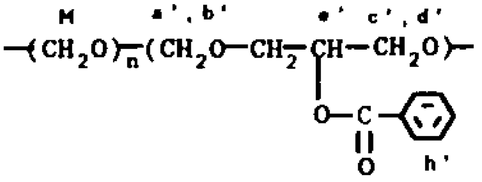
From GFA(α,β)



From GFA(α,α')

The incorporation of the two isomers in the same copolymer results in complex structural units with low spectral intensities (Fig. 3-13). A detailed study of a model copolymer is necessary to arrive at the complete assignment for copolymers GFA.

A copolymer of TOX with isomer GFB(α,α′) serves as such a model compound is :



From GFB(α,α')

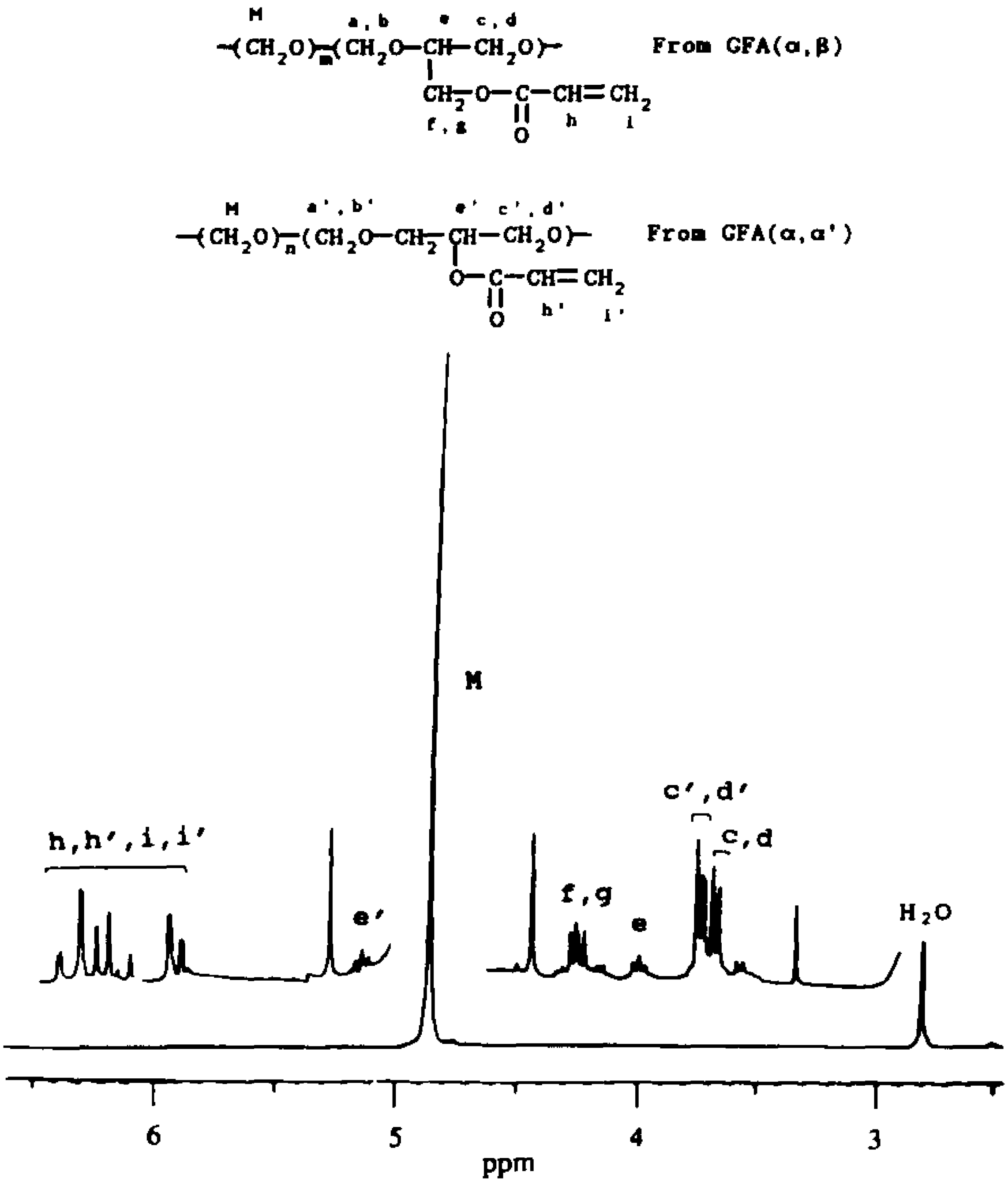


Fig. 3-13 ^{1}H NMR spectrum of copolymer GFA in DMSO-d_6 at 120 °C.

Fig. 3-14 shows a ^{1}H NMR spectrum of this copolymer. After ring opening, the two protons of **c′** and **d′** should be equivalent. Thus, the quartet from the monomer become a doublet in the copolymer (3.89 ppm). The proton **e′** is coupled to protons **c′** and **d′**, showing a multiplet at 5.30 ppm. The protons **a′** and **b′** after ring opening are submerged in the main peak of the units from TOX polymerization.

Comparing the NMR spectrum of copolymer GFA (Fig. 3-13) with that of copolymer GFB(α,α′) (Fig. 3-14), one can arrive at the spectral assignment for copolymer GFA. The ^{1}H absorptions due to incorporation of GFA(α,β) are: **c**,**d** (doublet, 3.65 ppm); **f**,**g** (multiplet, 4.10 - 4.35 ppm); **e** (multiplet, 3.8 - 4.05 ppm). Absorptions due to the incorporation of GFA(α,α′) is obvious based on the information from GFB(α,α′).

Once the **e′** absorption is identified, homonuclear decoupling experiment lead to complete spectrum assignment (Fig. 3-15). Spectrum 3-15A shows the original absorptions of the copolymer in the chemical shift range of interest. Decoupling of **e′** at 5.20 ppm, Fig. 3-15C, the absorptions of **c′** and **d′** turn into a singlet from a doublet. When proton **e** is irradiated, protons **c** and **d**, no longer coupled with **e**, showing a singlet absorption. Similarly, protons **f** and **g** now become an AB system, exhibiting a four-line absorption.

The assignments for ^{13}C NMR spectrum of copolymer GFA are based on information from ^{13}C NMR spectrum of copolymer GFB(α,α′) and comparison of proton decoupled spectrum with

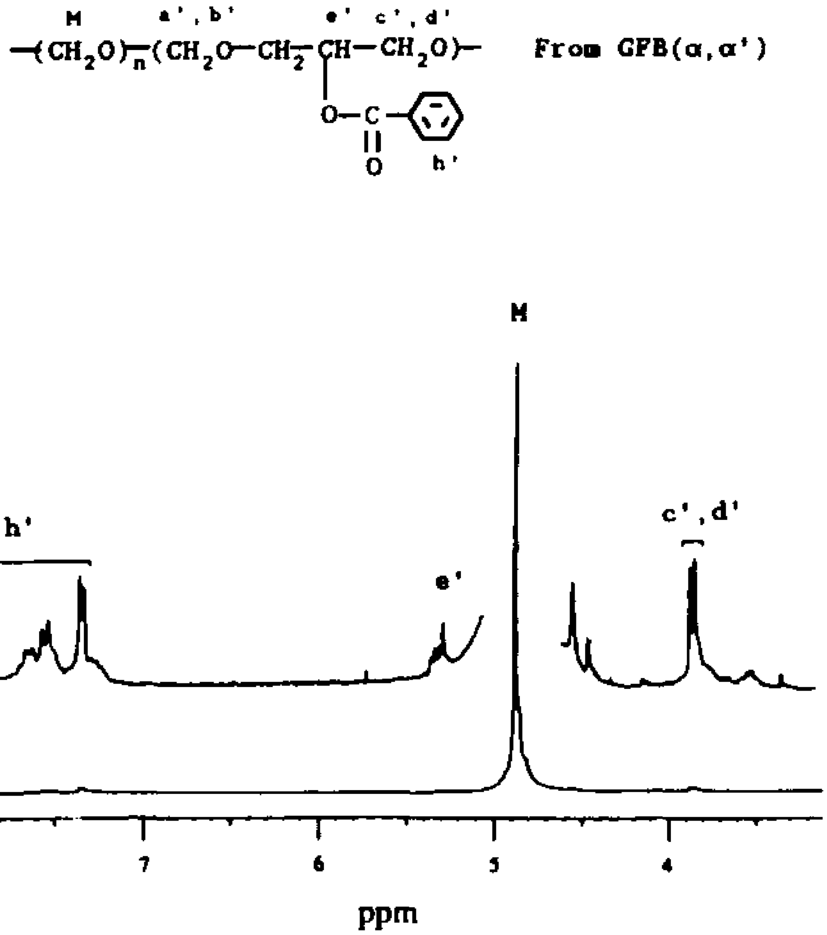


Fig. 3-14 ^{1}H NMR spectrum of copolymer GFB(α,α′) in DMSO-d_6 at 120 °C.

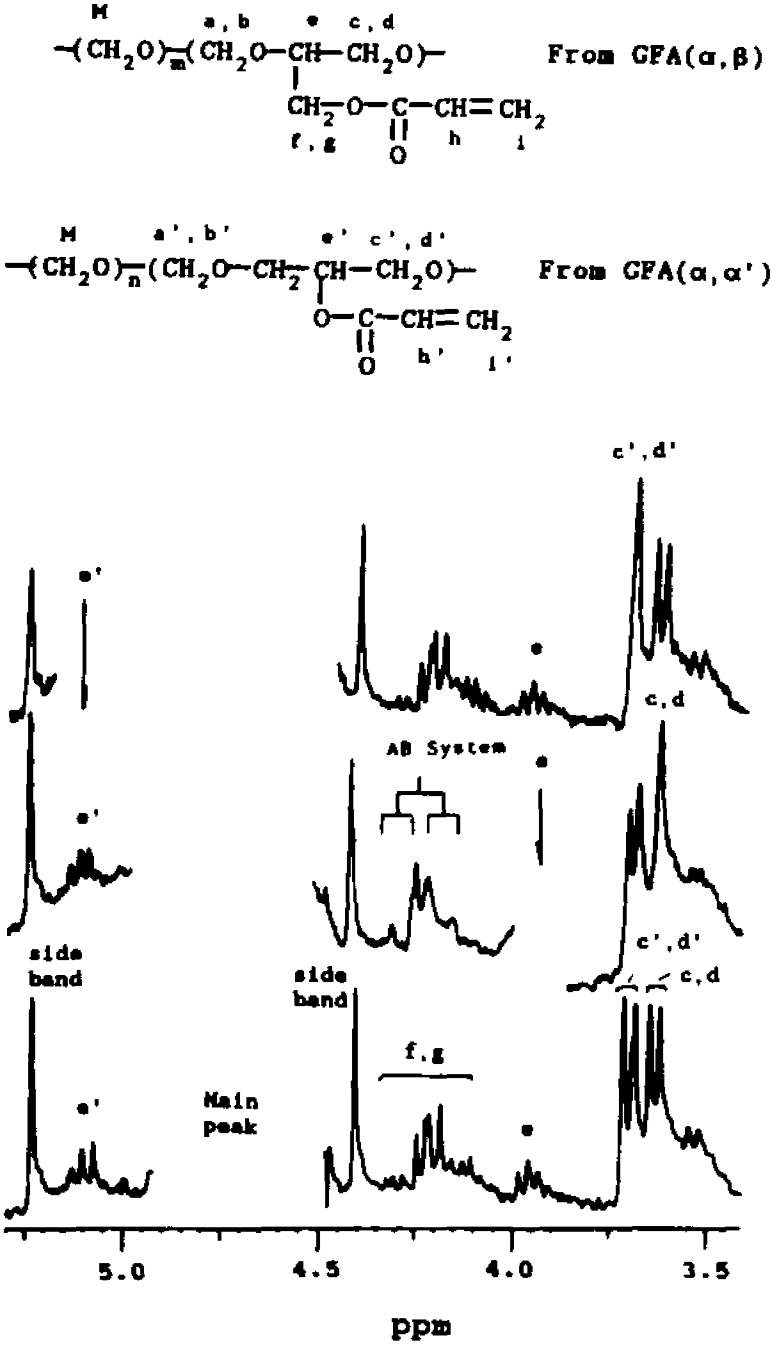
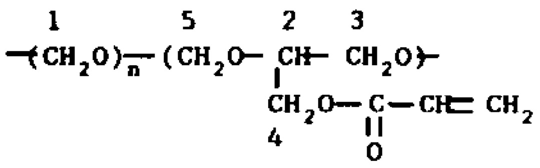


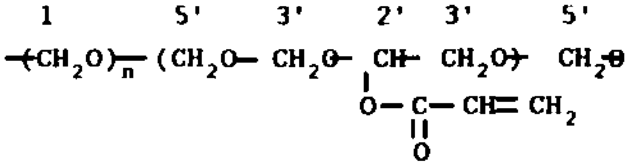
Fig. 3-15 Homonuclear decoupling ^1H NMR spectrum of copolymer GFA in DMSO-d_6 at 120 °C.

coupled ones. Based on a comparison of spectrum in Fig. 3-16d and spectrum in Fig. 3-16c, carbon-**3′** is shown to be connected to two protons; carbon-**2′** (72 ppm) to one protons; and carbon-**5′** (92.8 ppm), to two protons. The decoupled (Fig. 3-16a) together with the coupled (Fig. 2-16b) spectra for copolymer GFA show that carbons **2′** (71.5 ppm) and **3′** (66.5 ppm) are coupled to one and two protons respectively, matching **2′** and **3′** from GFB(α,α′). Therefore these are assigned to carbons from GFA(α,α′). Absorptions of carbons **2**, **3** and **4** must be then due to carbons from GFA(α,β). Their assignments are as follows: carbon **2**, coupled to one proton, corresponds to the methine group of the backbone; carbons 3, and **4**, each coupled with two protons, the methylene groups on the backbone and in the side chain next to the ester group respectively. Carbons **5** and **5′**, 91.5 and 92.8 ppm, each coupled to two protons, are assigned to unit from GFA(α,α′) and GFA(α,β) respectively. Absorption **5′** is stronger than that of **5**. There are two carbon **5′**; one from GFA(α,α′), the other from trioxane. There is only one carbon **5** for the structural unit:



$-(CH_2O)_n-(CH_2O-CH(CH_2O-C(=O)-CH=CH_2)-CH_2O)-$

GFA (α,β) unit



$-(CH_2O)_n-(CH_2O-CH_2O-CH(O-C(=O)-CH=CH_2)-CH_2O)-CH_2O$

GFA (α,α') unit

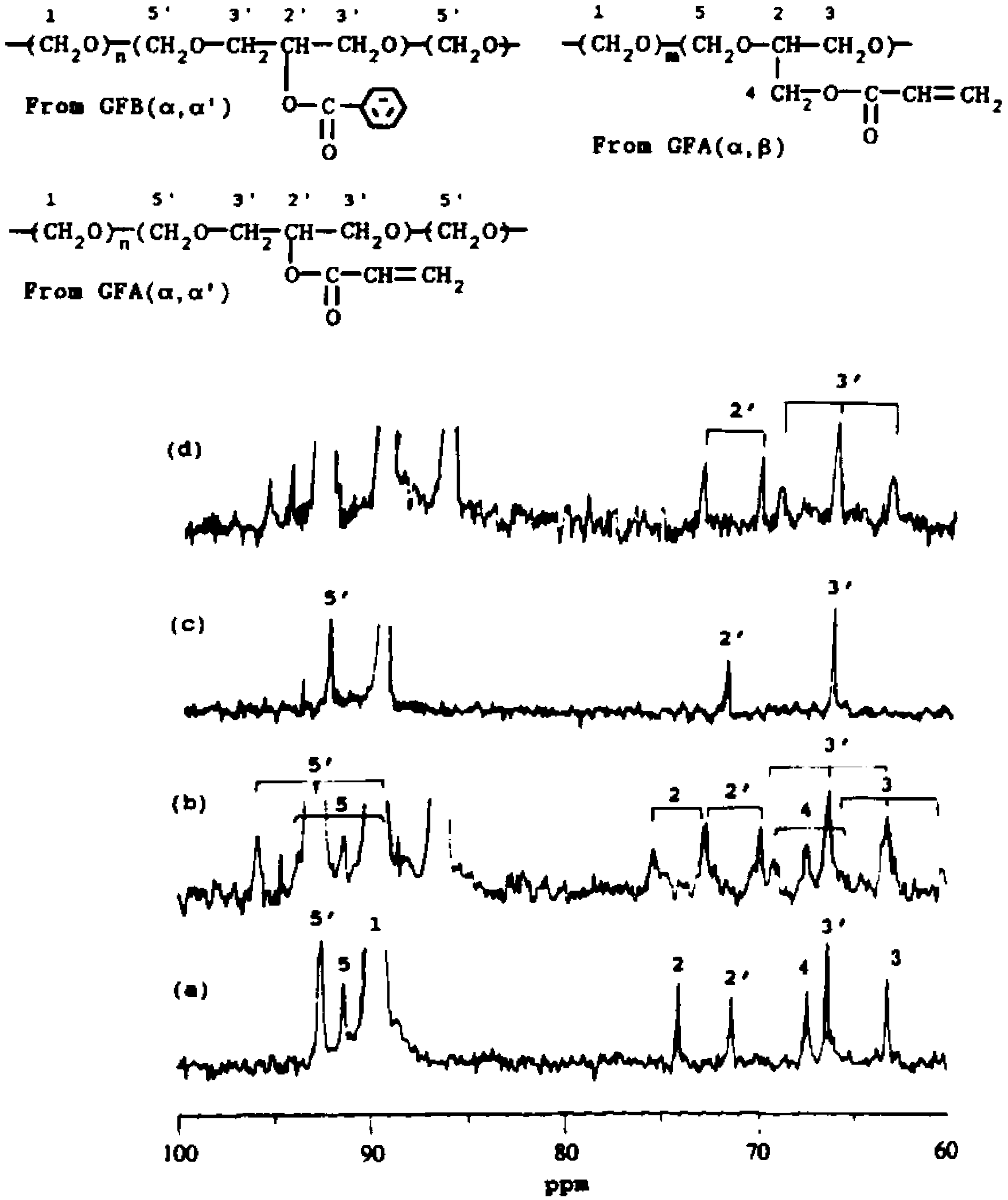


Fig. 3-16 Portion of ^{13}C NMR spectra of copolymer GFA in DMSO-d_6 at 120 °C.
(a) Decoupling Spectrum of copolymer GFA
(b) Coupling Spectrum of copolymer GFA
(c) Decoupling Spectrum of copolymer GFB(α,α')
(d) Coupling Spectrum of copolymer GFB(α,α')

(b) Incorporation ratio of isomers in Copolymer GFA.

The incorporation of isomers can be calculated based integrated intensity of copolymer on ^{1}H NMR spectrum (Fig. 3-13):

$$\underset{\text{(mole \%)}}{\alpha,\beta\text{-isomer incorporated}} = \frac{(c+d)/2}{(c+d)/2 + M/2} \times 100\%$$

$$\underset{\text{(mole \%)}}{\alpha,\alpha'\text{-isomer incorporated}} = \frac{(c'+d')/4}{(c'+d')/4 + M/2} \times 100\%$$

The double bond contents in copolymer is calculated from the equation:

$$\text{Double bond, mole \%} = \frac{(h + h' + i + i')/3}{(h + h' + i + i')/3 + M/2} \times 100\%$$

The experiment data show that the double bond incorporated is almost at the same level of the incorporation of GFA. The difference is less than 5%. Therefore the content of double bond is used to represent the incorporation of comonomer GFA.

The relative mole % of α,β-isomer incorporated can also be directly calculated from the ^{1}H NMR spectrum (Fig 3-13):

$$\begin{matrix}\%\ \alpha,\beta\text{-isomer}\\ \text{incorporated}\end{matrix} = \frac{(c+d)/2}{(c+d)/2 + (c'+d')/4} \times 100\% = 56\%$$

Isomer α,β, 43% in the GFA comonomer, is incorporated to a higher concentration level compared to isomer α,α'.

Apparently compared to the 6-member ring isomer GFA(α,α′), the 5-member ring of GFA(α,β) is ca.1.7 time, i.e. 56/44 x 57/43, more reactive in the ring-opening copolymerization with TOX initiated by $BF_3 \cdot OEt_2$.

(c) Effect of copolymerization conditions on the incorporation of GFA, molecular weight and yield.

For the copolymerization of TOX with GFA, the effects of reaction temperature, feed ratio and initiator content are significant. To prepare functionalized polyacetal copolymers for further reaction such as graft, concentration of reactive functionality of the macromolecules is an important parameter. For copolymers of trioxane with acrylate of 5-ethyl-5-hydroxymethyl-1,3-dioxane, an upper limit of 1.19% comonomer incorporation was determined (see section 2.3.4). For GFA monomer, up to 2.85 mole % may be incorporated. It was observed that a lower temperature of copolymerization leads to a higher GFA incorporation (Table 3-1). In the presence of GFA, the polymerization system initially can be kept in liquid form down to a temperature of 50°C. Lower copolymerization temperature results in lower rate of copolymerization and higher GFA incorporation.

A lower polymerization temperature also lead to high molecular weight and better final yield after hydrolysis. The molecular weight of the copolymer GFA is estimated by ^1H NMR spectroscopy assuming one $-OCH_3$ group for each chain, or determined from viscosity.

Table 3-1 Copolymerization of Trioxane with Glycerol Formal Acrylat

Sample	Reaction condition			Copolymer				
number	Temp. °C	$BF_3 \cdot EtO_2$ μl	Amine μl	Feed mol%	Incorp. mol%	Yield w%	Yield' w%	MW x10^{-3}
157A	69	20		5.95	0.54	91	47	4.9
157B	69	20		9.13	0.79	91	50	4.3
157C	69	20		12.5	1.00	88	56	5.3
158A	69	20		15.9	1.62	86	68	8.0
158B	69	20		19.6	1.70	79	61	4.9
160A	60	20	TPA/4	5.95	1.12	94	60	13.6
160B	60	20	TPA/4	9.13	1.18	95	56	3.0
160C	60	20	TPA/4	12.5	1.38	95	60	4.9
161A	60	20	TPA/4	15.9	1.72	93	61	5.7
161B	60	20	TPA/4	19.6	2.14	88	62	4.9
85	54	25	TEA/4	12.1	1.37	94	76	14
84	55	15	TEA/4	12.5	2.12	93	75	48
100	60	20	TPA/8	12.5	1.89	91	73	29
92	58	20	TPA/8	19.6	2.85	86	81	11
120	65	20	TPA/8	19.6	2.70	77	88	38
71	65	10	/	12.5	1.60	98	65	53

Yield: Copolymer washed with 1% TEA methanol solution
Yield': From base hydrolysis
MW: Determined from ^1H NMR, $-OCH_3$ group at 3.31 ppm.

The feed of comonomer GFA is a main factor in controlling the incorporation of GFA. As the feed of GFA is increased, the incorporation of GFA increases (Table 3-1). However, when the incorporation increases, the tendency to crosslink is higher. The crosslink may be due to the reaction of double bond initiated by cationic species as in the case of copolymer EMADO in section 2. The addition of tertiary amines prevents gel formation during copolymerization. In the absence of amine, copolymer formed may be a slightly crosslinked. A high double bond incorporation in the copolymer can lead to crosslinking. The addition of tertiary amines to the copolymerization system gives a better control over the process. Two amines, triethyl- and tripropyl- amines, were tested. Tripropylamine seems more effective due to its higher boiling point. The amine was added before the injection of initiator. The addition of amines not only prevent gel formation, but also lower the rate of copolymerization and increase the incorporation.

The effect exerted by the amines may originate from their interaction with the boron-trifluoride initiator. The amines are stronger base than the ether in the initiator complex and thus can form a stronger complex with BF_3. A more stable BF_3 complex is less reactive, leading to a slower cationic copolymerization with higher GFA incorporation.

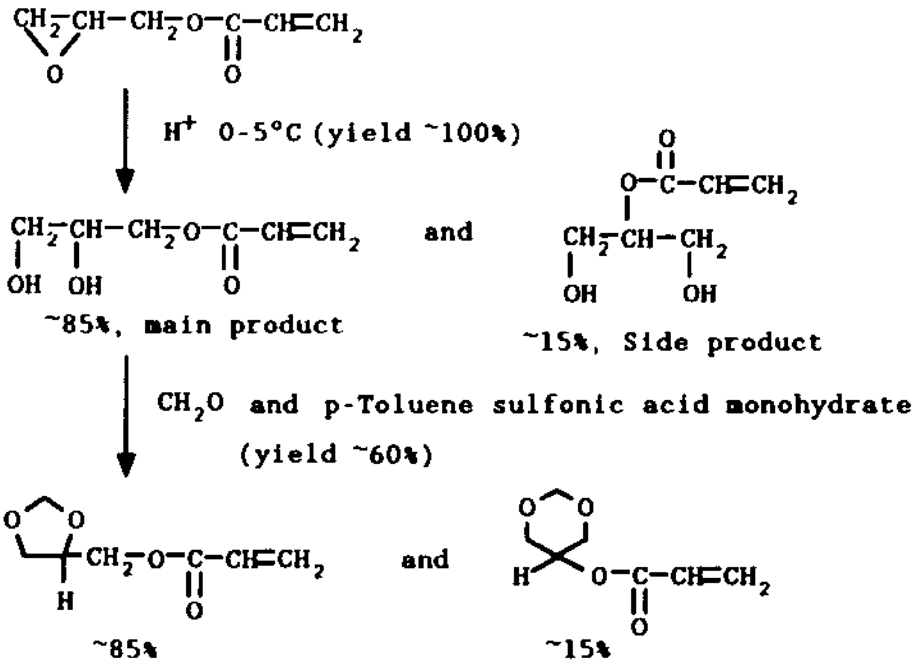
Other factors, such as water content in the system, may affect the copolymerization. It is believed that lower content of water leads to a lower copolymerization rate and poor GFA incorporation.

(d) Copolymerization of trioxane with GFB and GFAc

Copolymers GFB and GFAc were synthesized by copolymerization of trioxane with comonomer GFB and GFAc respectively through similar procedures as copolymer GFA.

3.3.6. Synthesis of 1,3-dioxolane-4-methyl acrylate (α,β-isomer of GFA)

Glycidyl acrylate can be readily converted quantitatively to 1,2-dihydroxyl-propyl acrylate (1,2-diol) in the presence of H^+ at 0 - 5 °C in aqueous solution. Fig. 3-17 shows a ^1H NMR spectrum of the product. The multiplet at 5.84 - 6.40 ppm due to the double bond in acrylate group. The proton **c** in methine group coupled with two methylene groups leads to a multiplet at 3.68-3.82 ppm. A doublet at 3.40-3.46 ppm is assigned to the protons **a** and **b** in methylene connected to a hydroxyl group. A multiplet at 4.00-4.20 ppm is due to the protons **d** and **e** of methylene group connected to the acrylate group. There are a multiplet and a quartet at 4.82 and 3.60 ppm respectively due to a side product shown below:



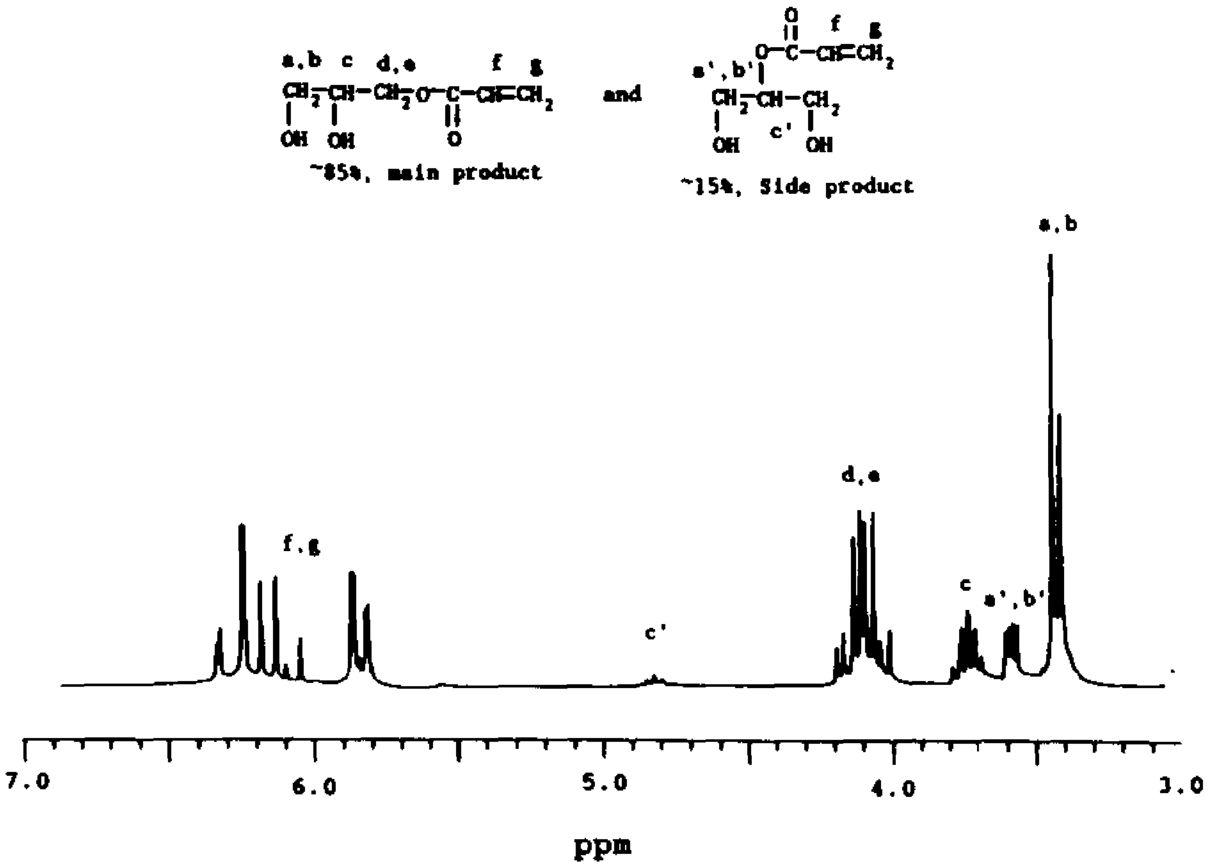
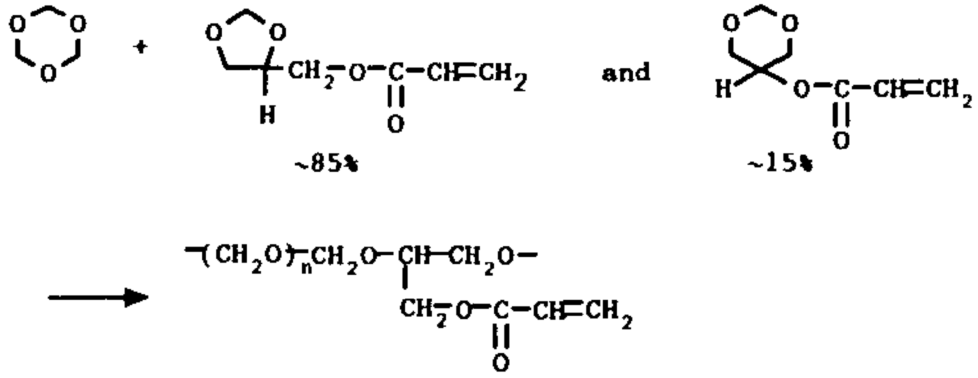


Fig. 3-17 ^1H NMR spectrum of 1,2-dihydroxyl-propyl-acrylate in DMSO-d_6 at 120°C.

The main product 1,2-diol is about 85% and the side product 15% determined from the ^1H NMR spectrum (Fig. 3-17). Reaction of diol with paraformaldehyde in the presence of p-toluene sulfonic acid monohydrate gives 1,3-dioxolane-4-methyl acrylate with 15% of side-product, 1,3-dioxane-5-acrylate. Fig. 3-18 shows a ^1H NMR spectrum of the product and the assignment which matches the assignment of GFA.

3.3.7. Copolymer of TOX with 1,3-dioxolane-4-methyl acrylate (copolymer GFA(α,β))

Fig. 3-19 shows a ^1H NMR spectrum and assignment of copolymer of trioxane with 1,3-dioxolane-4-methyl acrylate copolymer, designated as copolymer GFA(α,β).



The assignment is the same as copolymer GFA, but the α,α′-isomer units in copolymer is at a low level about 10 mole % in the total incorporation. This copolymer can be hydrolyzed to obtain copolymer GF(α,β) (see next section).

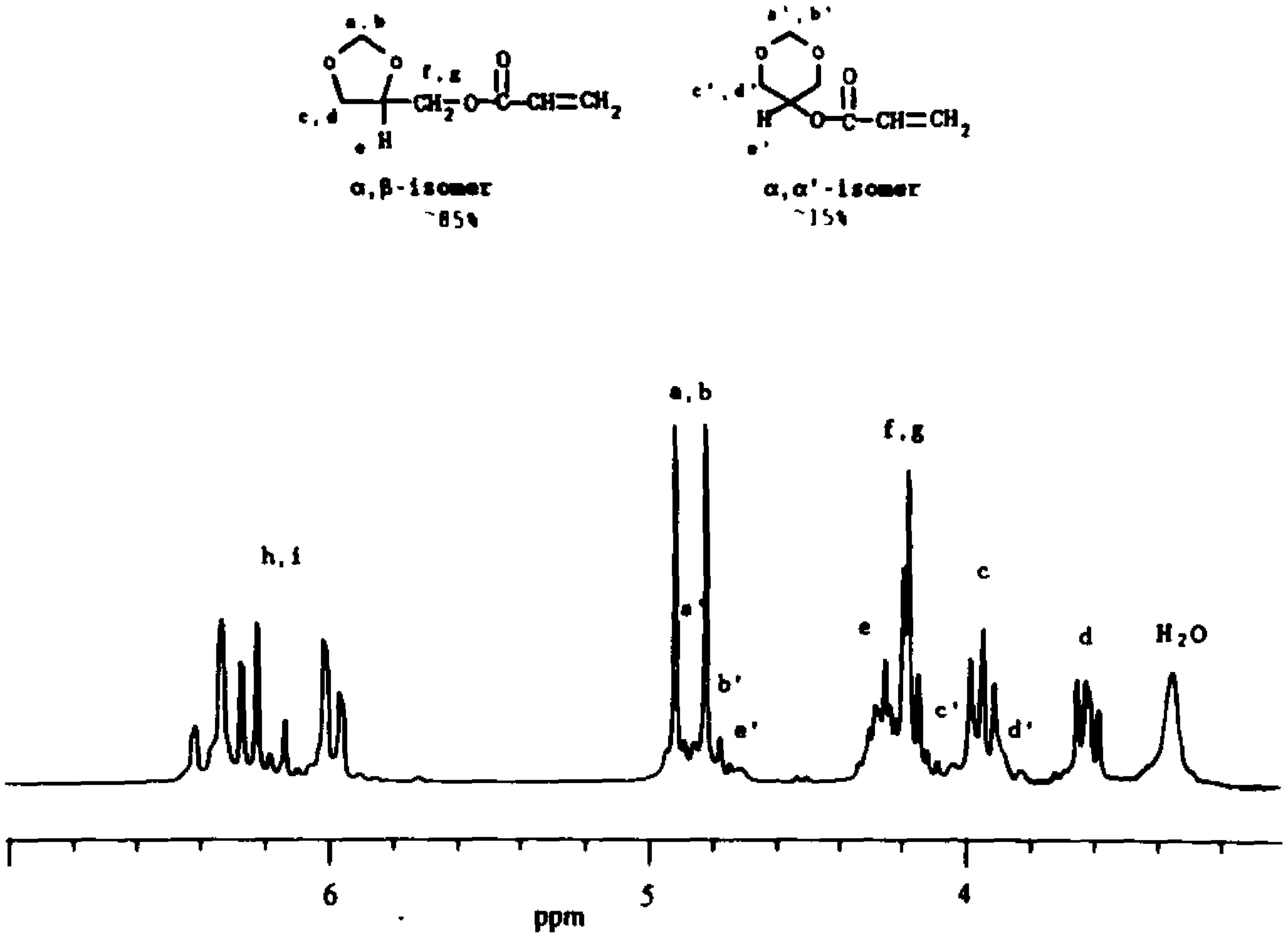


Fig. 3-18 ^1H NMR spectrum of 1,3-dioxolane-4-methyl acrylate in DMSO-d_6 at 120°C.

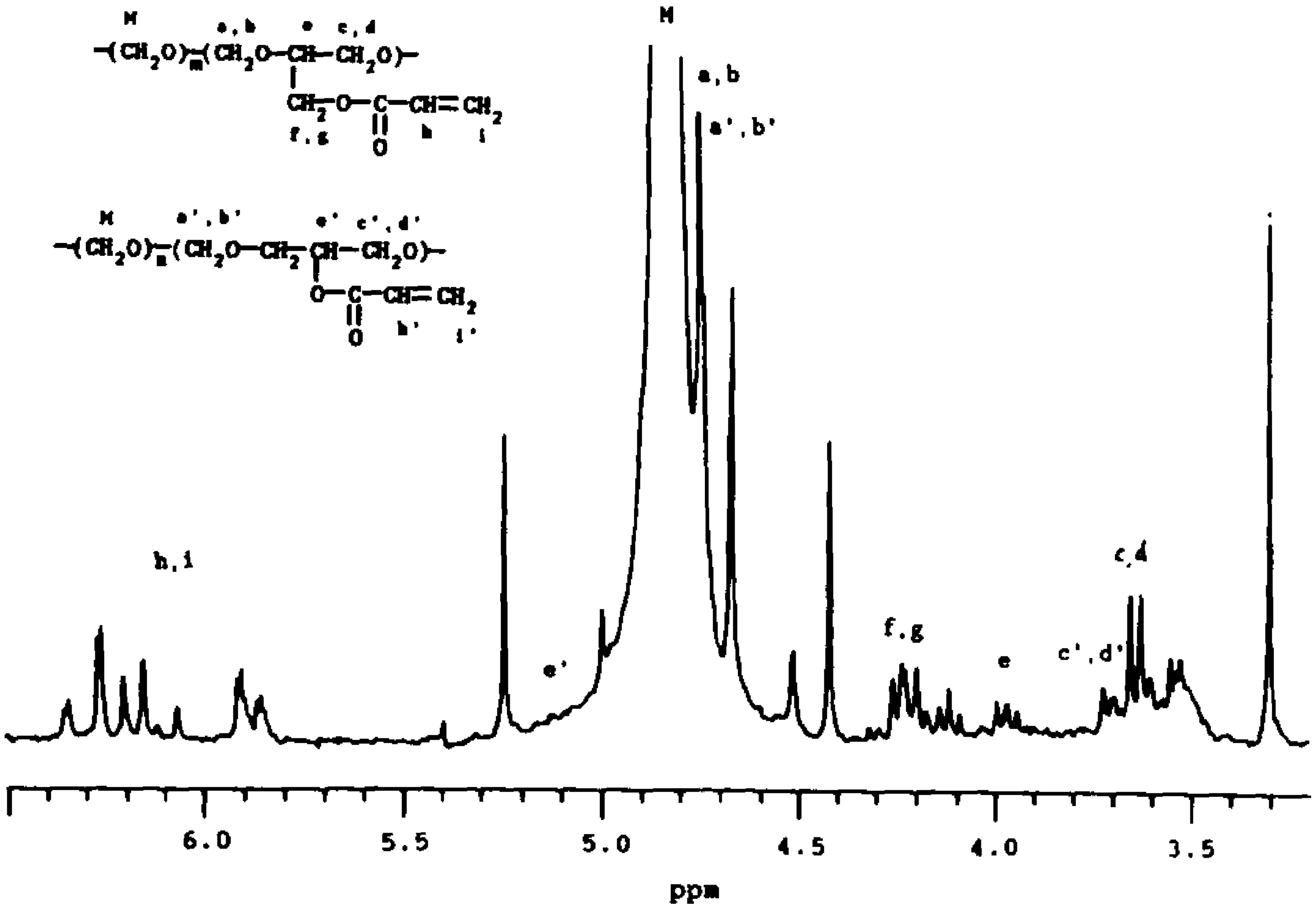
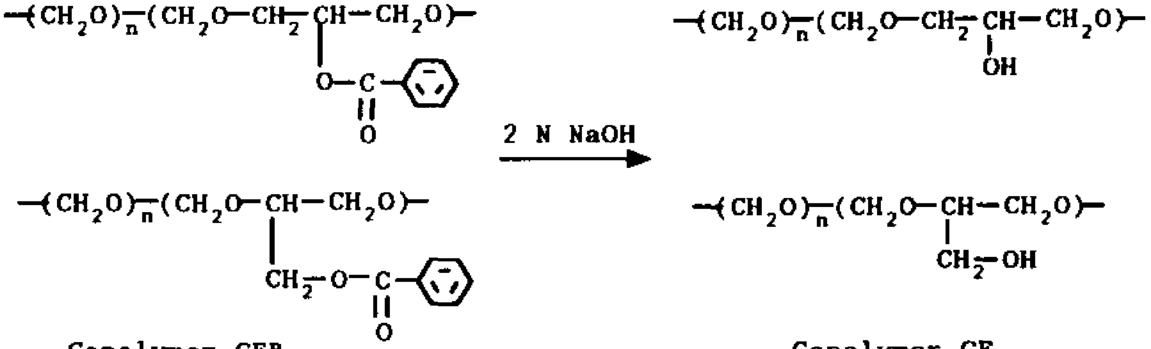


Fig. 3-19 ^{1}H NMR spectrum of copolymer of trioxane with 1,3-dioxolane-4-methyl acrylate in DMSO-d_6 at 120°C.

3.3.8. Preparation of glycerol formal copolymer with high level of pendant hydroxyl functionality.

Comonomer GF can be copolymerized with trioxane to form copolymer. However, high molecular weight copolymers can not be obtained, due to hydroxyl groups of GFA functioning as a very effective chain transfer group$^{(4)}$. A high molecular weight of copolymer GF are obtained through hydrolysis of copolymer GFB (or GFAc):



Copolymer GFB

Copolymer GF

The yield of base hydrolysis was 80-90%.

Fig. 3-20 shows a ^{1}H NMR spectrum of copolymer GF obtained from above process. The aromatic group at 7.20 - 7.50 ppm was no longer observed, indicating the efficient hydrolysis of the ester group. The multiplets at 3.35 - 3.90 ppm are complicated due to the spectral overlap of the two isomeric systems.

Fig. 3-21 shows a ^{1}H NMR spectrum of copolymer GF(α,α′) obtained from copolymer GFB(α,α′) using above process. The multiplet at 3.81 ppm is assigned to proton **e′**; the peak at 3.53 ppm to protons **c′** and **d′**. Fig. 3-22 shows a ^{1}H NMR

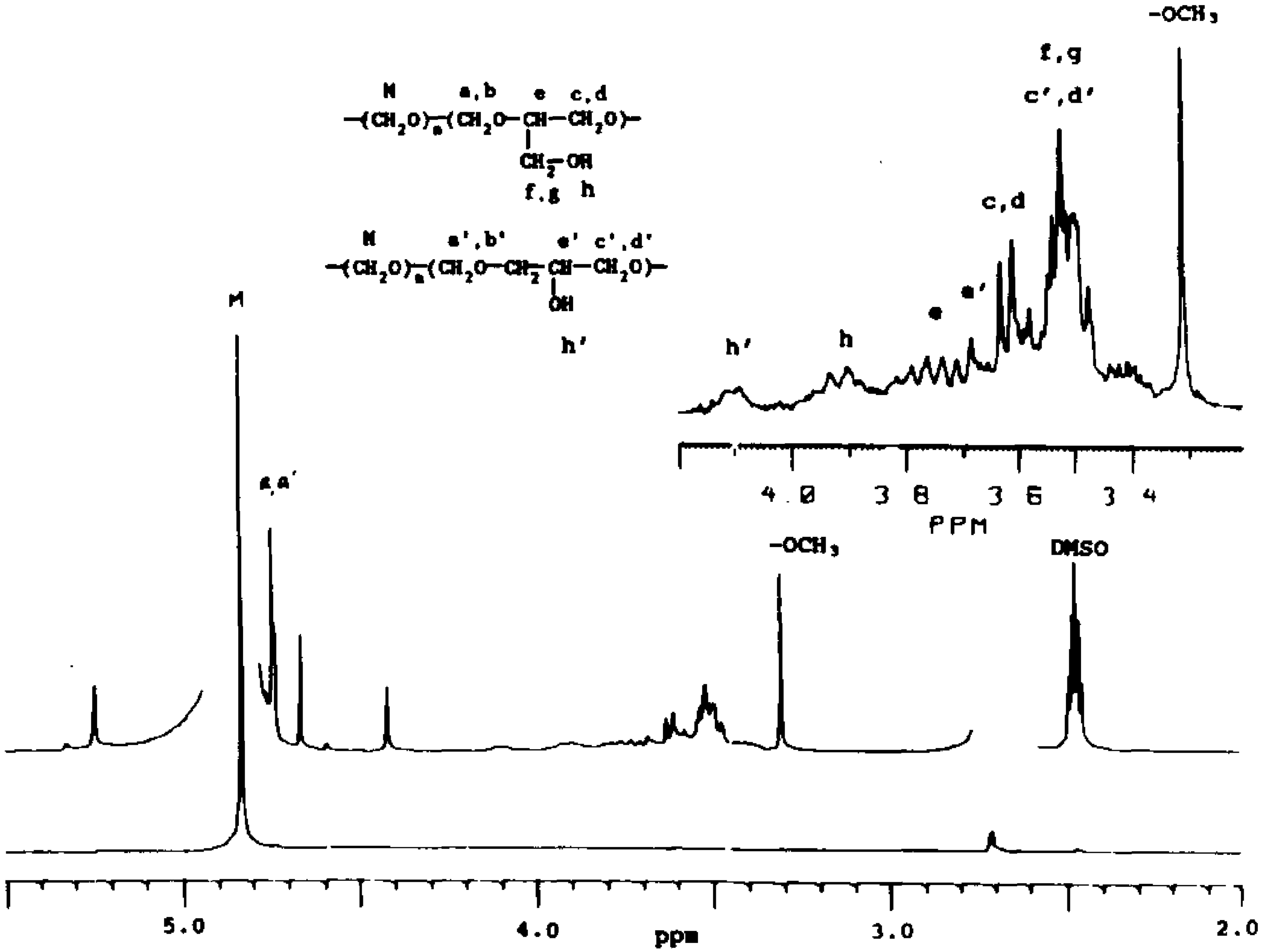


Fig. 3-20 ^1H NMR spectrum of copolymer GF in DMSO-d_6 at 120°C.

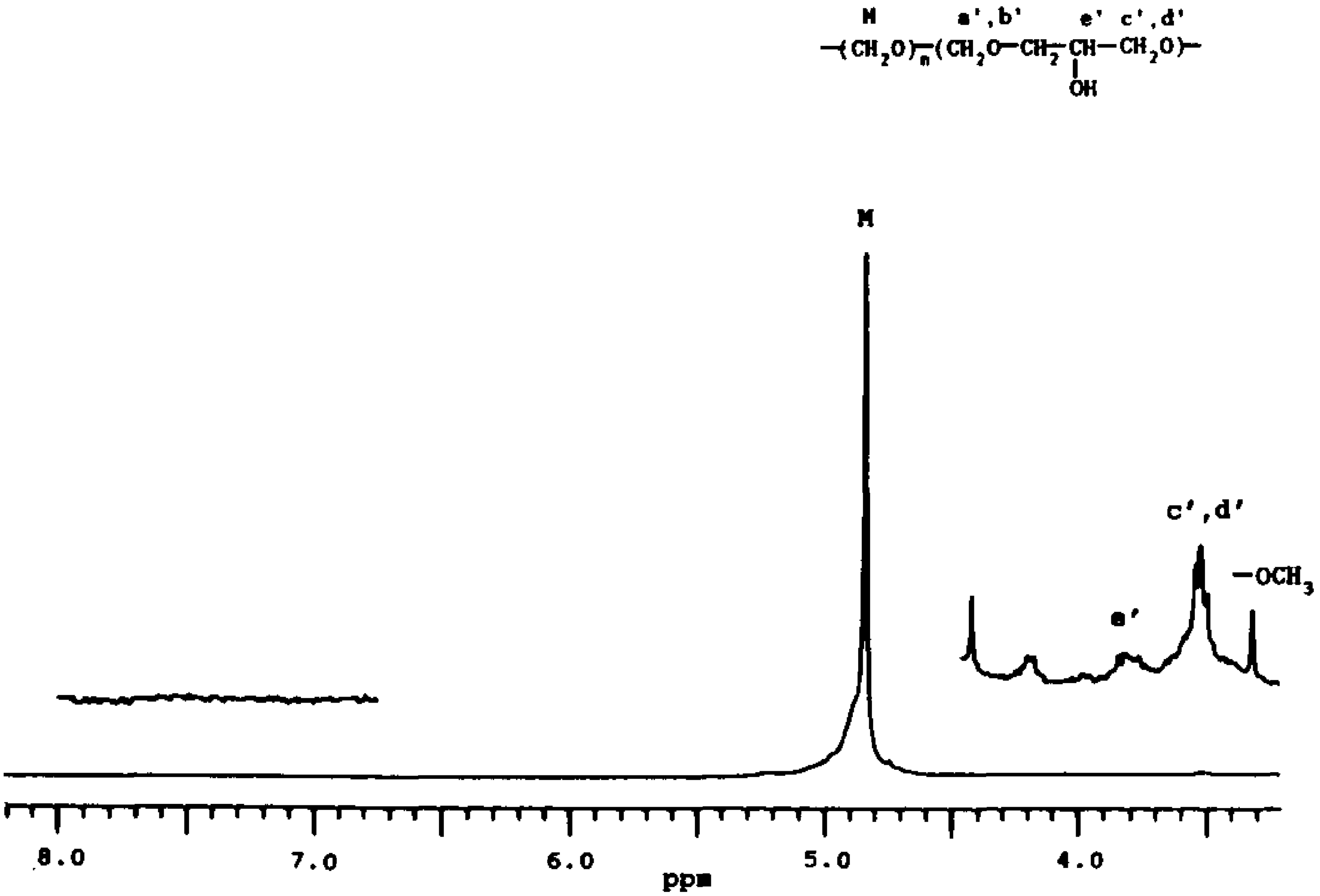


Fig. 3-21 ^{1}H NMR spectrum of copolymer GF(α,α') in DMSO-d_6 at 120°C.

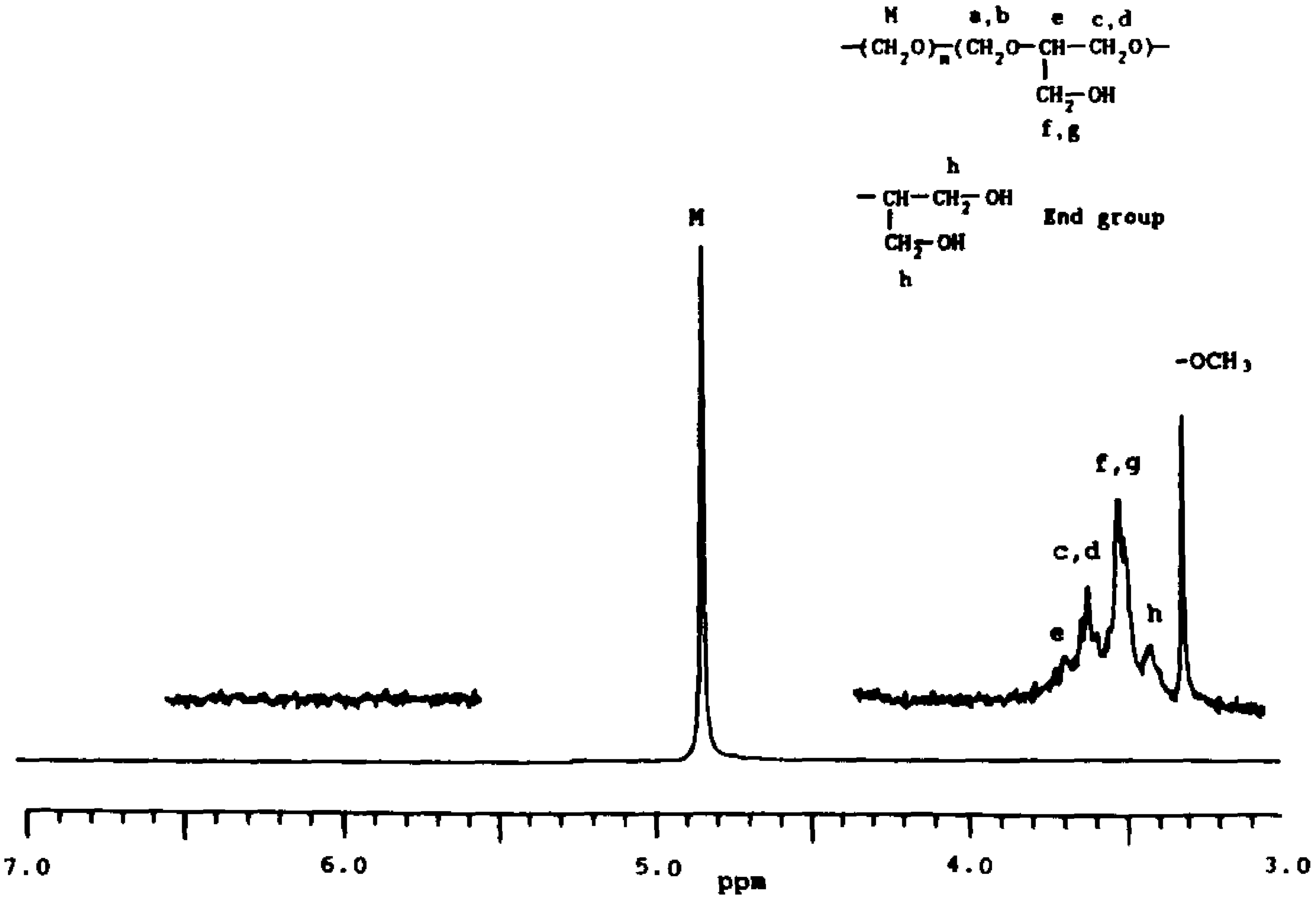
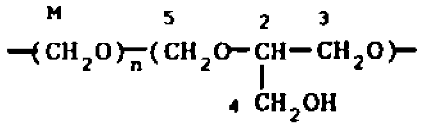


Fig. 3-22 ^{1}H NMR spectrum of copolymer GF(α,β) in DMSO-d_6 at 120°C.

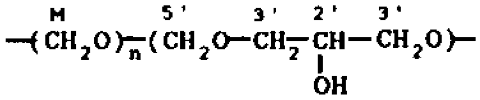
spectrum of copolymer GF(α,β) hydrolyzed from copolymer GFA(α,β). The multiplet at 3.71 ppm is assigned to proton **e**; the peak at 3.64 ppm to protons **c** and **d**. A doublet at 3.52 ppm is due to protons **f** and **g**. The combination of these two spectra gives the assignment of copolymer GF as shown in Fig. 3-20.

Fig. 3-23 shows a ^{13}C NMR spectrum of copolymer GF from copolymer GFB. The copolymer GF contains two isomeric units GF(α,β) and GF(α,α′):



$$\overset{M}{-(CH_2O)_n}-(\overset{5}{CH_2}O-\underset{\underset{4}{CH_2OH}}{\overset{2}{CH}}-\overset{3}{CH_2}O)-$$

Copolymer GF(α,β) unit

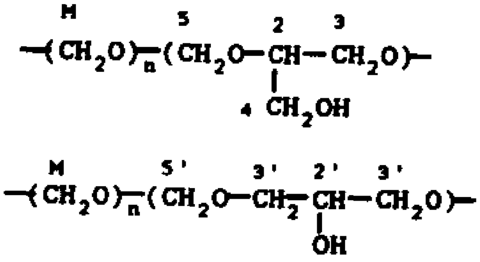


$$\overset{M}{-(CH_2O)_n}-(\overset{5'}{CH_2}O-\overset{3'}{CH_2}-\underset{OH}{\overset{2'}{CH}}-\overset{3'}{CH_2}O)-$$

Copolymer GF(α,α') unit

The main peak at 89.8 ppm is due to $-(CH_2O)_n-$ from trioxane in copolymer. The peaks at 91.38, 77.16. 67.88 and 60.66 ppm are due to carbon-**5**, -**2**, -**4** and -**3** from copolymer GF(α,β) unit respectively. The peaks at 92.53, 69.52 and 68.15 ppm are due to carbon-**5′**, -**3′** and -**2′** respectively from copolymer GF(α,α′) unit.

This assignment is further substantiated by a distortionless enhanced polarization transfer, DEPT, experiment on the copolymer GF(α,α′) hydrolyzed from copolymer GFB(α,α′). Fig. 3-24 shows a DEPT spectrum of copolymer GF. The negative peaks at 92.53, 91.38 and 89.90 ppm are due to $-CH_2-$. The positive peaks at 77.16 and 68.15



$$-\!\left(\overset{M}{CH_2O}\right)_{n}\!-\!\left(\overset{5}{CH_2O}-\underset{4\ CH_2OH}{\overset{2}{CH}}-\overset{3}{CH_2O}\right)\!-$$

$$-\!\left(\overset{M}{CH_2O}\right)_{n}\!\left(\overset{5'}{CH_2O}-\overset{3'}{CH_2}-\underset{OH}{\overset{2'}{CH}}-\overset{3'}{CH_2O}\right)\!-$$

Chemical shift (ppm)	
M	89.7
5	91.4
2	77.2
3	67.9
4	60.7
5'	92.5
3'	69.6
2'	68.2

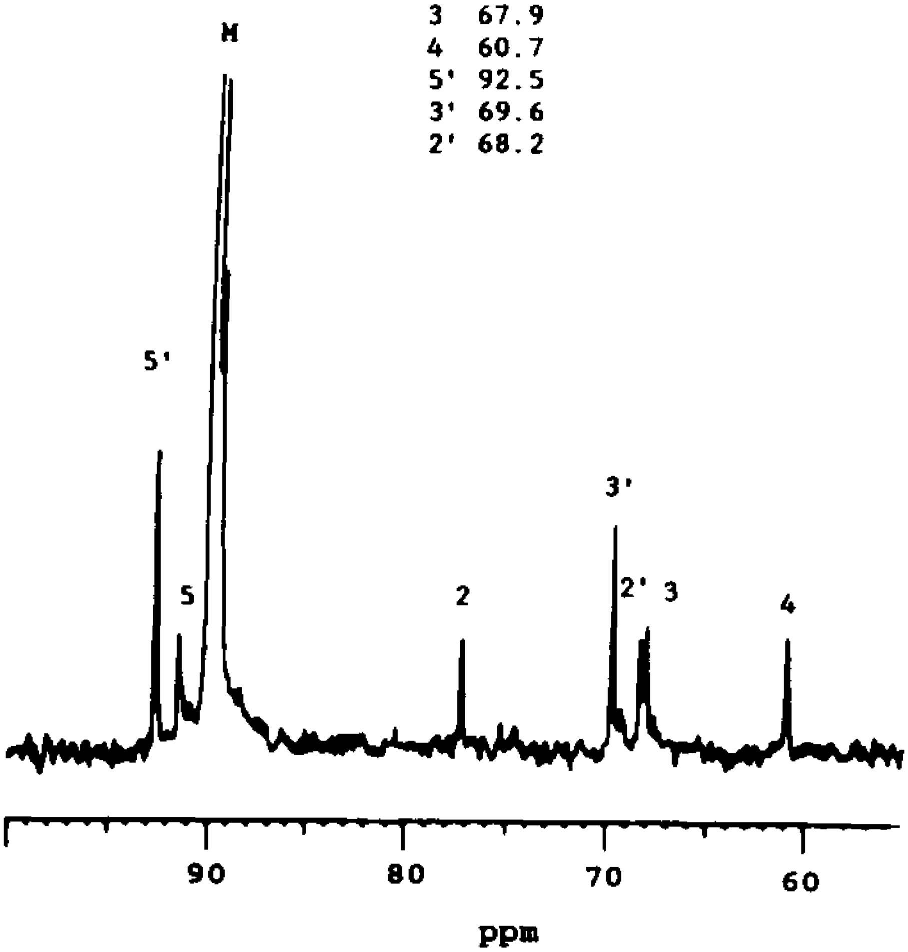
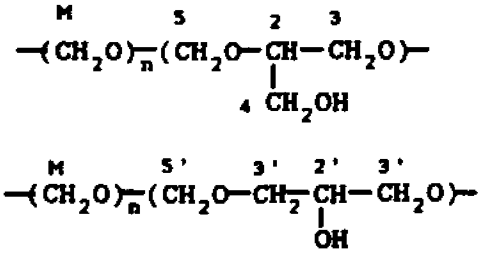


Fig. 3-23 ^{13}C NMR spectrum of copolymer GF in DMSO-d_6 at 120°C.



$$-(\overset{M}{CH_2O})_n-(\overset{5}{CH_2}O-\overset{2}{\underset{\overset{|}{{}_4\,CH_2OH}}{CH}}-\overset{3}{CH_2}O)-$$

$$-(\overset{M}{CH_2O})_n-(\overset{5'}{CH_2}O-\overset{3'}{CH_2}-\overset{2'}{\underset{\overset{|}{OH}}{CH}}-\overset{3'}{CH_2}O)-$$

Chemical shift (ppm)	
M	89.7
5	91.2
2	77.0
3	67.7
4	60.5
5'	92.5
3'	69.6
2'	68.2

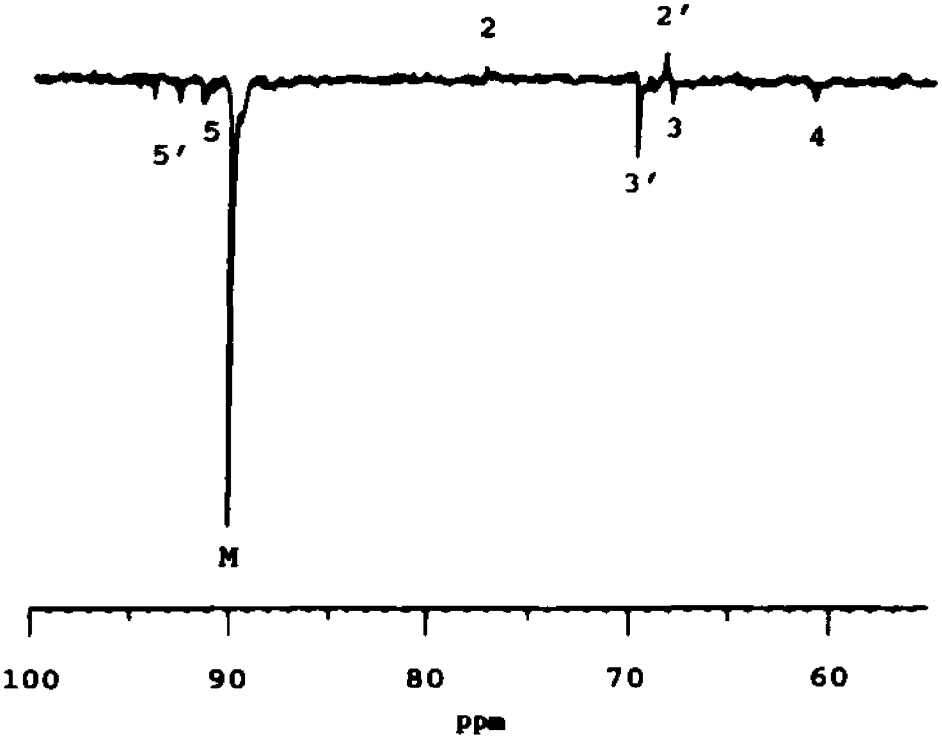
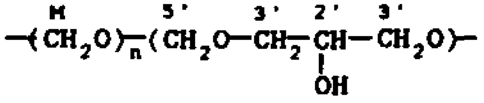


Fig. 3-24 DEPT NMR spectrum of copolymer GF in DMSO-d_6 at 120°C.



$$\overset{M}{-(CH_2O)_n}-(\overset{5'}{CH_2}O-\overset{3'}{CH_2}-\underset{OH}{\overset{2'}{CH}}-\overset{3'}{CH_2}O)-$$

Chemical shift (ppm)

M	89.7
5'	92.5
3'	69.6
2'	68.2

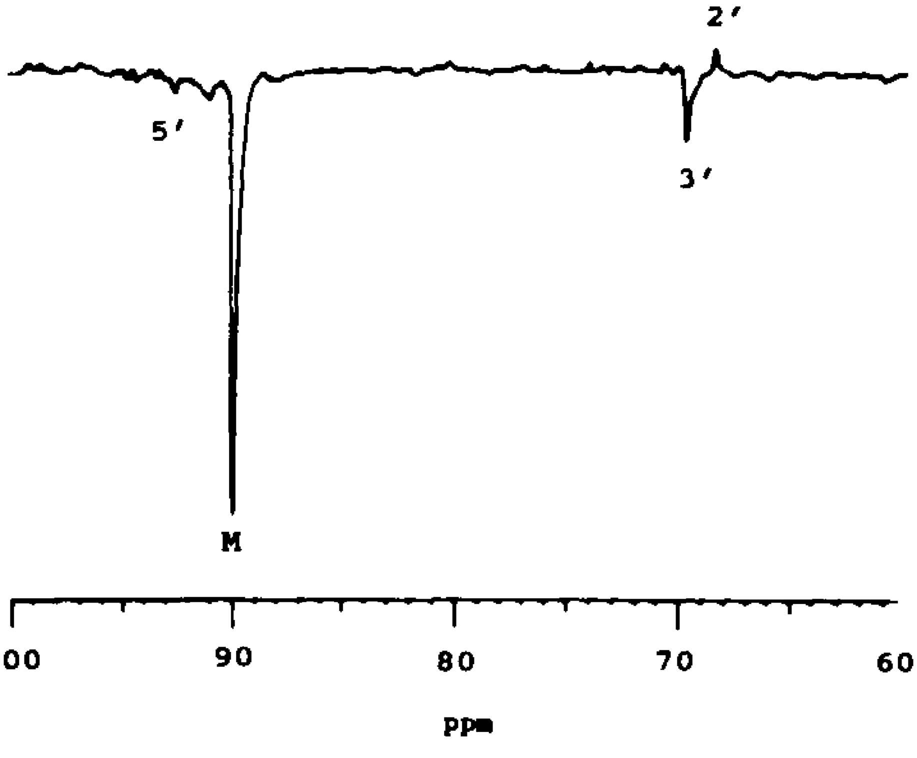


Fig. 3-25 DEPT NMR spectrum of copolymer GF(α,α') in DMSO-d_6 at 120°C.

ppm are due to -CH- group (or CH_3, but no CH_3 in the polymer). Fig. 3-25 shows a DEPT NMR spectrum of copolymer GF(α,α'), indicating that the peaks at 68.5 (CH), 69.52 (CH_2) and 92.53 (CH_2) are due to the (α,α') isomer unit.

3.3.9. Graft of copolymer GFA

The copolymer GFA has been prepared in the molecular weight range of 3 x 10^3 to 4 x 10^4 with pendant double bond up to 2.85 mole %. The double bond was shown to be reactive toward amine and stable against base hydrolysis in the presence of hydroquinone. It is a better candidate for the preparation of polyacetal graft copolymer than the copolymer EMADO in Section 2.

For copolymer GFA, up to 95% of the double bond functional groups remains in the final purified copolymer product. For further reaction with copolymers, the reactivity of the double bond is also important. For a 5 ml N,N-dimethylacetamide, DMAc, solution of 0.5 g copolymer GFA with ca 1.84 mole % of double bond, heating at 170°C leads to gel formation within 10 minutes. When 20 mg of hydroquinone, a free radical reaction inhibitor, was added, no gel was observed within 3 hrs. Thus, one can carry out the grafting reaction without running the risk of forming crosslink network under these conditions. Fig. 3-26 shown a ^1H NMR spectrum of copolymer GFA grafted with dodecylamine at 170 °C in DMSO for 30 min.; all double bonds have

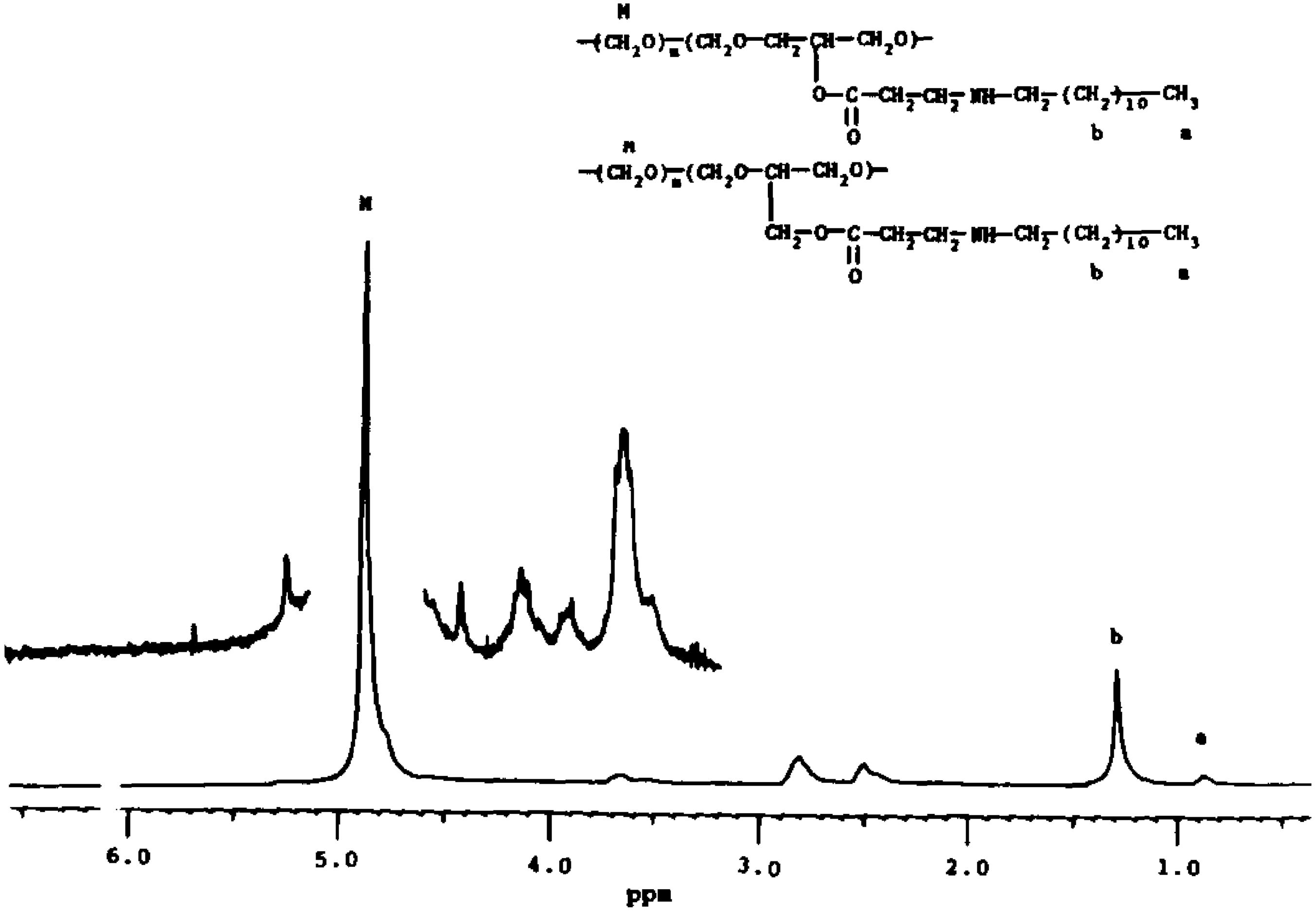
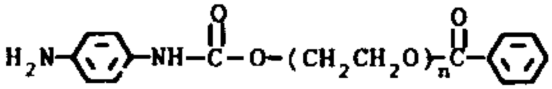


Fig. 3-26 ^{1}H NMR spectrum of copolymer GFA grafted with dodecylamine in DMSO-d_6 at 120°C.

reacted. Thus, the copolymer GFA has been demonstrated to be a good candidate for the preparation of polyacetal graft copolymer.

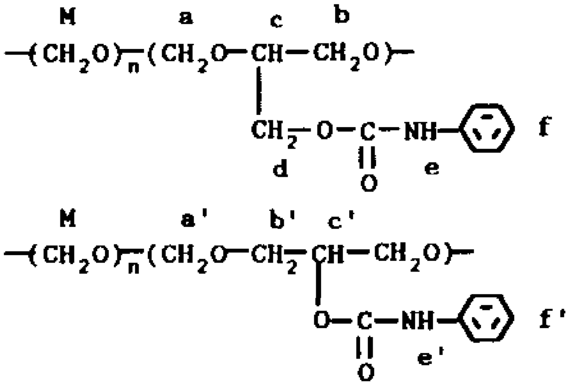
An amine endcapped polyethylene glycol (PEG-NH_2) with molecular weight of 600 was used for graft reaction with copolymer GFA. The structure of PEG-NH_2 is shown below:



The graft copolymer is used to study the crystallinity of copolymer.

3.3.10. Graft of copolymer GF

Fig. 3-27 shows a ^{1}H NMR spectrum of copolymer GF grafted with phenylisocyanate.



The spectrum of the graft copolymer is quite different from that of copolymer GF (Fig. 3-20) but resembles the spectrum of copolymer GFA (Fig. 3-13), since their main structures

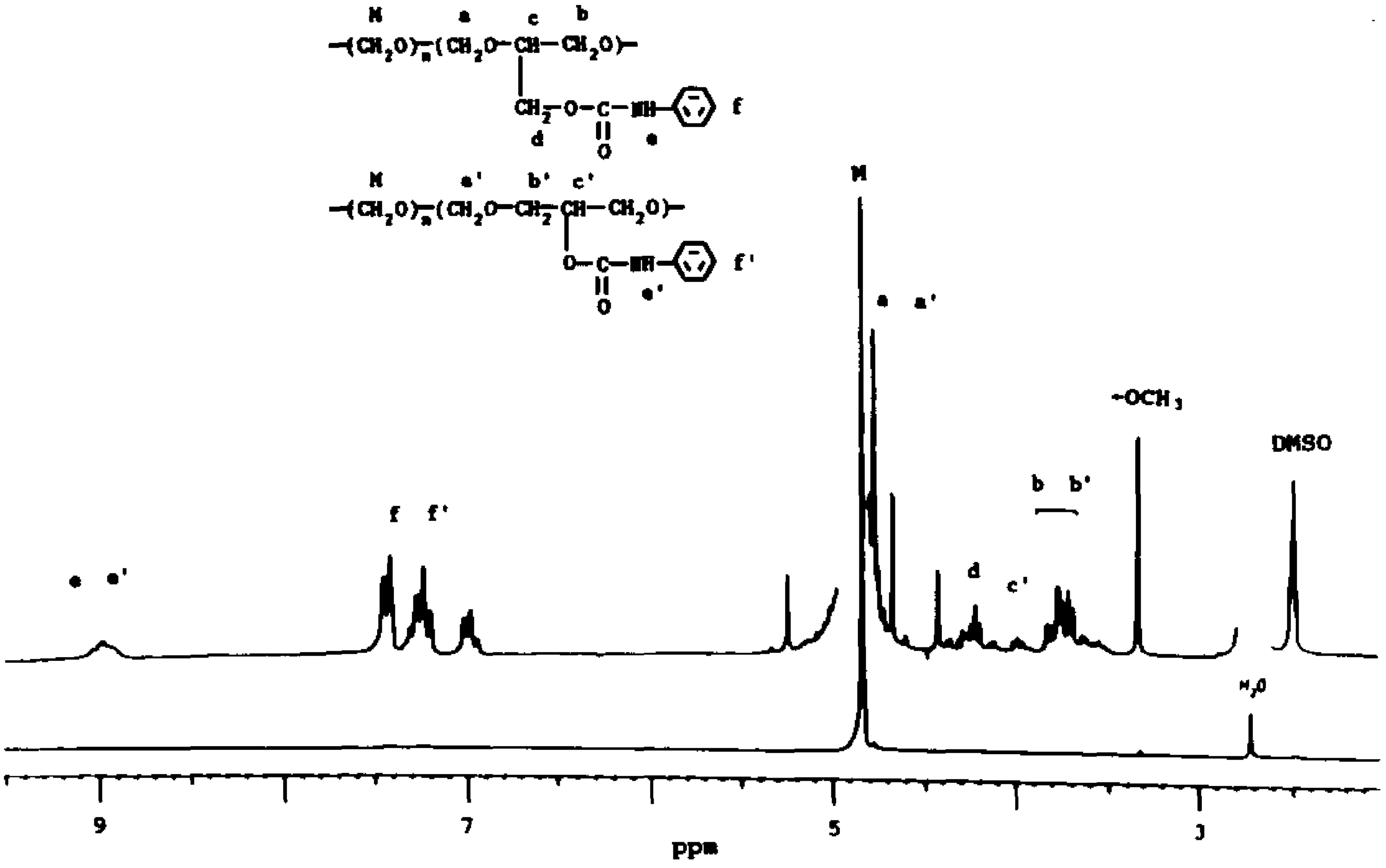


Fig. 3-27 ^{1}H NMR spectrum of copolymer GF grafted with phenylisocyanate in DMSO-d_6 at 120°C.

are the same. The multiplet at 6.9 - 7.6 ppm due to the aromatic group and the main peak at 4.84 ppm due to $(CH_2O)_n$ can be used to calculate the incorporation of grafted phenylisocyanate. In this sample of Fig. 3-27, 2.0 mole % of phenylisocyanate was grafted.

3.3.11. Thermal Stability of copolymers

TGA thermograms of copolymer GF and GFA, homopolymer of trioxane and copolymer of trioxane with ethylene oxide clearly establish the stability of the copolymers. No degradation of copolymer took place at temperature lower than 220 °C.

3.3.12. Crystallinity of copolymers

Fig. 3-29 is a typical DSC curve of copolymer GFA (sample 157BB). There are two endotherms at 160.96 °C and 165.92 °C. The latter is usually taken as the melting point of copolymer. Table 3-2 summarizes the crystallinity and the melting point of copolymers. The melting point of homopolymer of trioxane is as high as 171°C, however; the melting point of copolymers decreases with the increase in incorporation of comonomer of GFA. For instance, the melting point of copolymer GFA is only 158 °C when the incorporation of GFA is 2.14 mole % in copolymer.

Two representations of crystallinity are given: Apparent crystallinity is based on the total sample weight and reduced crystallinity is based on the weight of

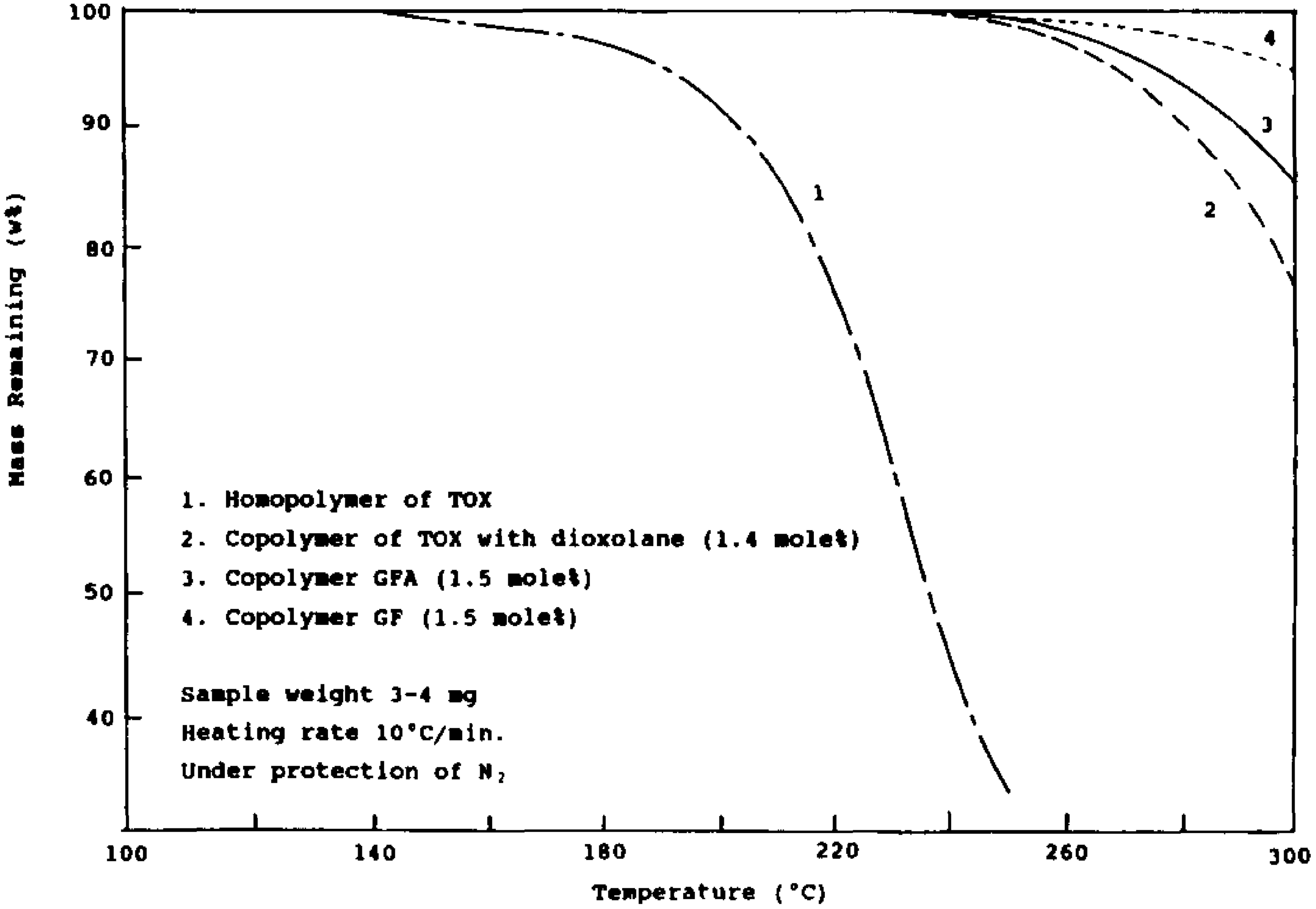


Fig. 3-28 TGA thermograms of copolymers

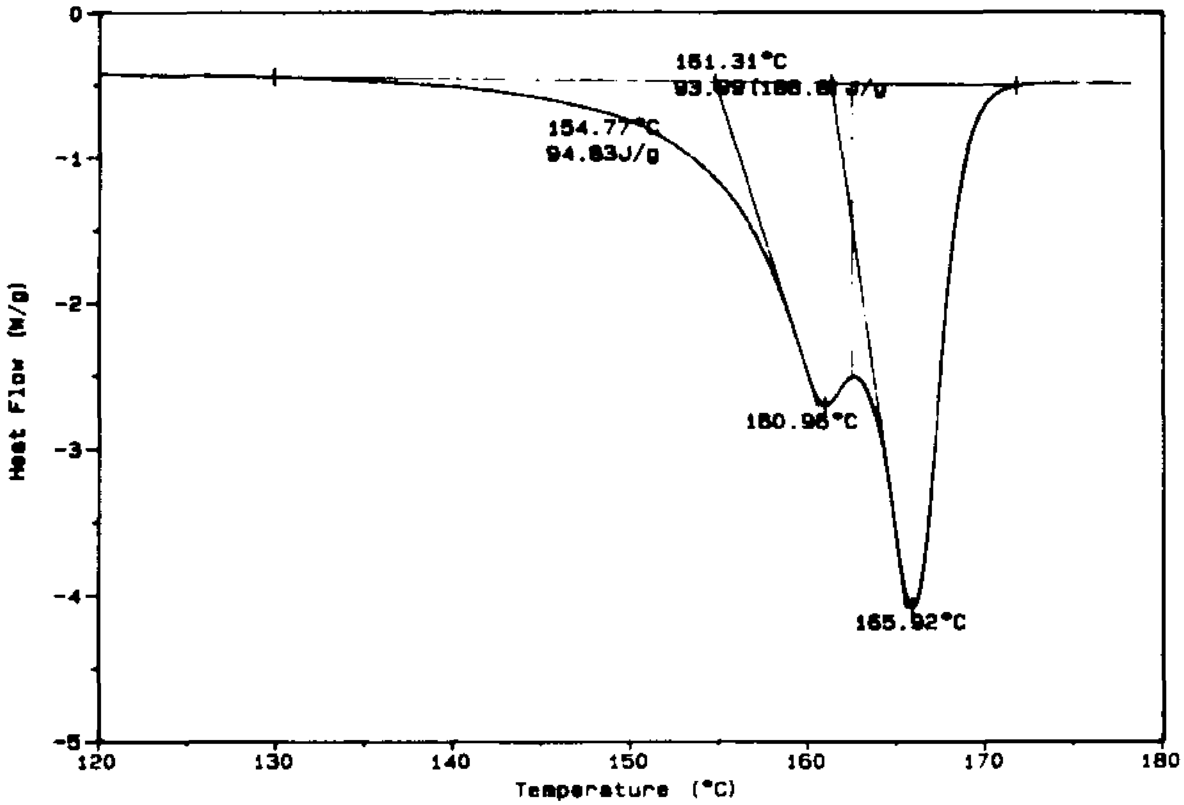


Fig. 3-29 DSC curves of copolymer GFA.

Table 3-2 Effects of Comonomers on Crystallinity of Copolymers

Sample No.	Comonomers	Incorp. of GFA		Crystallinity, %		melting point °C
		mole %	Weight %	Appparent	Reduced	
157AA	GFA	0.54	2.78	71±1	73±1	167±1
157BB	GFA	0.79	4.02	76±1	79±1	165±1
157CC	GFA	1.00	5.32	70±1	74±1	163±1
160AA	GFA	1.12	5.97	68±1	72±1	164±1
160BB	GFA	1.18	6.29	69±2	74±2	165±1
160CC	GFA	1.38	7.37	67±1	72±1	163±1
158AA	GFA	1.62	8.67	70±2	76±2	161±1
158BB	GFA	1.70	9.11	68±1	75±1	160±1
161AA	GFA	1.72	9.22	68±2	74±2	162±1
161BB	GFA	2.14	10.3	63±2	70±2	158±3
133	Homopolymer	0	0	85±2	85±2	171±1
93	Dioxolane	7.0	17.8	63±1	76±1	151±1
120	GFA	2.8	13.5	63±2	73±2	155±1

methylene oxide units only. The latter is calculated by assuming that comonomer units were not incorporated in crystal cell and can not contribute to the heat of fusion. For example, the apparent crystallinity of copolymer of trioxane with dioxolane with 7.0 mole % (17.8 W %) of incorporation is 63 %, the reduced crystallinity then is:

$$\text{Reduced Crystallinity} = \frac{\text{Apparent crystallinity}}{100 - \text{weight \% of comonomerincorporated}} \times 100$$

$$= \frac{63}{100 - 17.8} \times 100 = 76\ \%$$

The reduced crystallinity of copolymer are all lower than that of homopolymer from table 3-2.

The melting point used in this study are from the second melting peak as shown in Fig. 3-29. Flory's equation for copolymer is used to analyze the relationship between the melting point of copolymer and the mole fraction of formaldehyde using the data in Table 3-2:

$$(1/T_m) - (1/T_m^\circ) = -(R/\Delta H_f)\ln X_a$$

where T_m° —— melting temperature of trioxane homopolymer
T_m —— Melting point of copolymer
R —— Gas constant, 8.31 J/K·mole
ΔH_f —— Heat of fusion
X_a —— Mole fraction of formaldehyde units

Fig.3-30 shows the relationship between $(1/T_m)$ and $-\ln X_a$. A straight line was obtained with the intercept of 2.260 and slope of 0.002574. The correlation coefficient is 0.9229. The melting point of homopolymer calculated from the intercept is 170°C, consistent with the determined melting point (171°C) in Table 3-2. The heat of fusion calculated from the slope is 107.6 J/g, deviating greatly from the literature value[5] (245.4 J/g).

Table 3-3 shows the effect of graft on crystallinity of

Table 3-3 Effects of Graft on Crystallinity of Copolymer GFA

Sample No.	Incorp. of GFA		Grafting			Crystallinity, %		Melting point, °C
	mole %	Weight %	Graft	M%	W%	Appparent	Reduced	
120	2.85	13.5				63±2	73±2	155±1
89A	2.85	13.5	PEA	1.8	7.5	50±1	58±1	146±1
89C	2.85	13.5	PEA	2.0	8.1	46±1	53±1	149±1
80A	2.85	13.5	PEG	1.3	7.9	43±1	50±1	151±1
80B	2.85	13.5	PEG	2.8	16.4	39±1	46±1	149±1
80C	2.85	13.5	PEG	5.4	27.3	31±1	37±1	144±1

PEA, Phenethylamine
PEG, PEG-amine

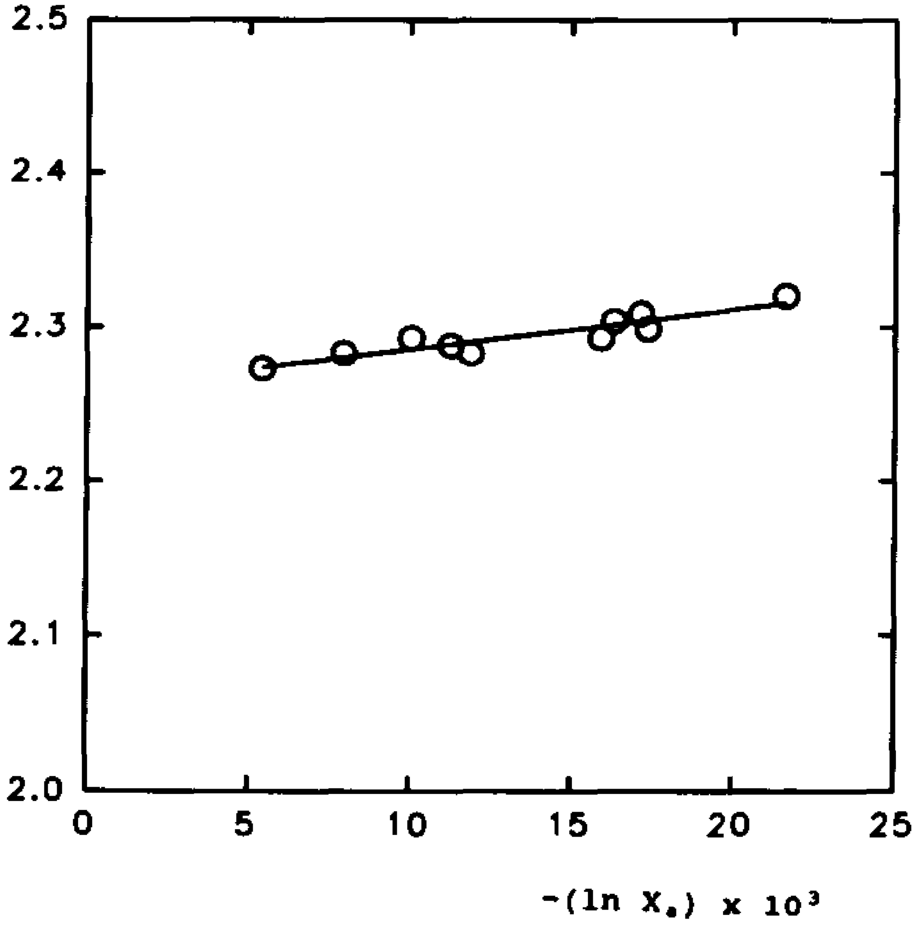


Fig. 3-30 Relationship between melting point and fraction of formaldehyde units

T_m: Melting point of copolymers

X_a: Fraction of formaldehyde units

copolymer GFA. There were two different graft side chains: PEA, phenethylamine (MW 121); PEG-NH_2 (MW 600). The crystallinity of graft copolymers depends on the incorporation and molecular weight of graft side chain. A higher graft content leads to a lower crystallinity. A higher molecular weight of graft side chain gives a lower crystallinity. The lower reduced crystallinity implies that the comonomer units not only does not incorporate into crystal cell, but also obstruct its neighbor units of CH_2O to enter the crystal cell, resulting in lower crystallinity.

The properties of the blends of copolymer-type polyacetals with polyurethane (PU) were investigated[6]. Table 3-4 shows the original data from the paper except the columns C(%)* and C(%)**:

Table 3-4 Heat of Fusion (H_f), Degree of Crystallinity (X_c) and Melting Temperature at peak (T_m) for the Blend

Blend Composition	H_f(J/g)	C(%)*	X_c(%)	Reduced C(%)**	T_m(°C)
0% PU	162.8	66.3	63.2	63.2	161.6
10% PU	143.1	58.3	55.4	61.6	161.5
25% PU	115.4	47.0	46.0	61.3	161.1
50% PU	86.6	35.3	30.8	61.6	160.5

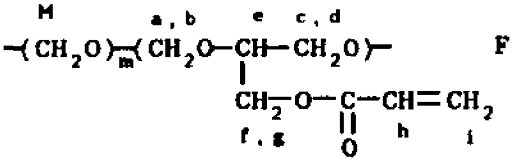
C(%)*—— Crystallinity calculated from heat of fusion (H_f), using ΔH_f = 58.7 cal/g (245.4 J/g) for 100% of crystallinity.

Reduced C(%)**—— Calculated from crystallinity obtained from X-ray diffraction study.

The crystallinity calculated from heat of fusion (H_f) determined from DSC and the crystallinity obtained from X-ray diffraction study are in good agreement, the crystallinity from DSC is consistent with that obtained from X-ray diffraction. The reduced crystallinity C(%)** calculated from X-ray data are very close to that of 0% PU sample. This indicates that in the blend PU do not affect the crystallinity of polyacetal itself. The melting points of all four blends remain mainly unchanged. However, the presence of graft side chain in present study decreases the crystallinity and the melting point of acetal copolymers systems.

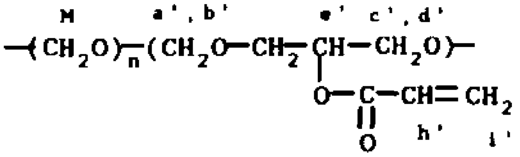
3.4. Conclusion

The copolymerization of trioxane with the isomeric mixture of glycerol formal acrylate, GFA, gives copolymers with the two different structural units:



$$-(CH_2O)_m(CH_2O-\underset{\displaystyle CH_2-O-\underset{\displaystyle O}{\overset{\|}{C}}-CH=CH_2}{CH}-CH_2O)-$$

From GFA(α, β)



$$-(CH_2O)_n(CH_2O-CH_2-\underset{\displaystyle O-\underset{\displaystyle O}{\overset{\|}{C}}-CH=CH_2}{CH}-CH_2O)-$$

From GFA(α, α')

The complete assignments for the ^{1}H NMR spectra of the comonomers as well as the copolymers have been accomplished. The ^{1}H NMR data thus established allow detailed quantification of the copolymerization process for all glycerol formal esters. For the acrylate comonomers, the 5-membered ring α,β-isomer is shown to be ca. 70% more reactive than the 6-membered ring α,α′-isomer in cationic copolymerization.

For GFA comonomers, lower copolymerization temperature gives better comonomer incorporation, higher yield and higher molecular weight. As much as 2.85 mole % of double bond can be incorporated into the polyacetal copolymers. The addition of tertiary amines to the system suppresses the crosslinking reaction through the double bond during copolymerization. The presence of added low concentration of hydroquinone reduces gel formation during both the hydrolysis of copolymer as well as the reaction of grafting polyamide onto the copolymer GFA. The acrylate in copolymers is demonstrated to be reactive toward both primary and secondary amines.

A copolymer with structure equivalent to the copolymer of trioxane with glycerol formal was obtained from the hydrolysis of copolymer of trioxane with glycerol formal benzoate or glycerol formal acetate in NaOH solution at 95-100°C in heterogeneous system. This reaction suggested that the comonomer units are on the surface of polymer crystal or the amorphous area of copolymer. The hydroxyl groups were shown to be reactive toward isocyanates.

Both comonomer units GFA and GF are shown to serve as stable end groups and unzipping stoppers. DSC study of copolymers shows that the copolymer and the graft copolymer have lower melting point and crystallinity.

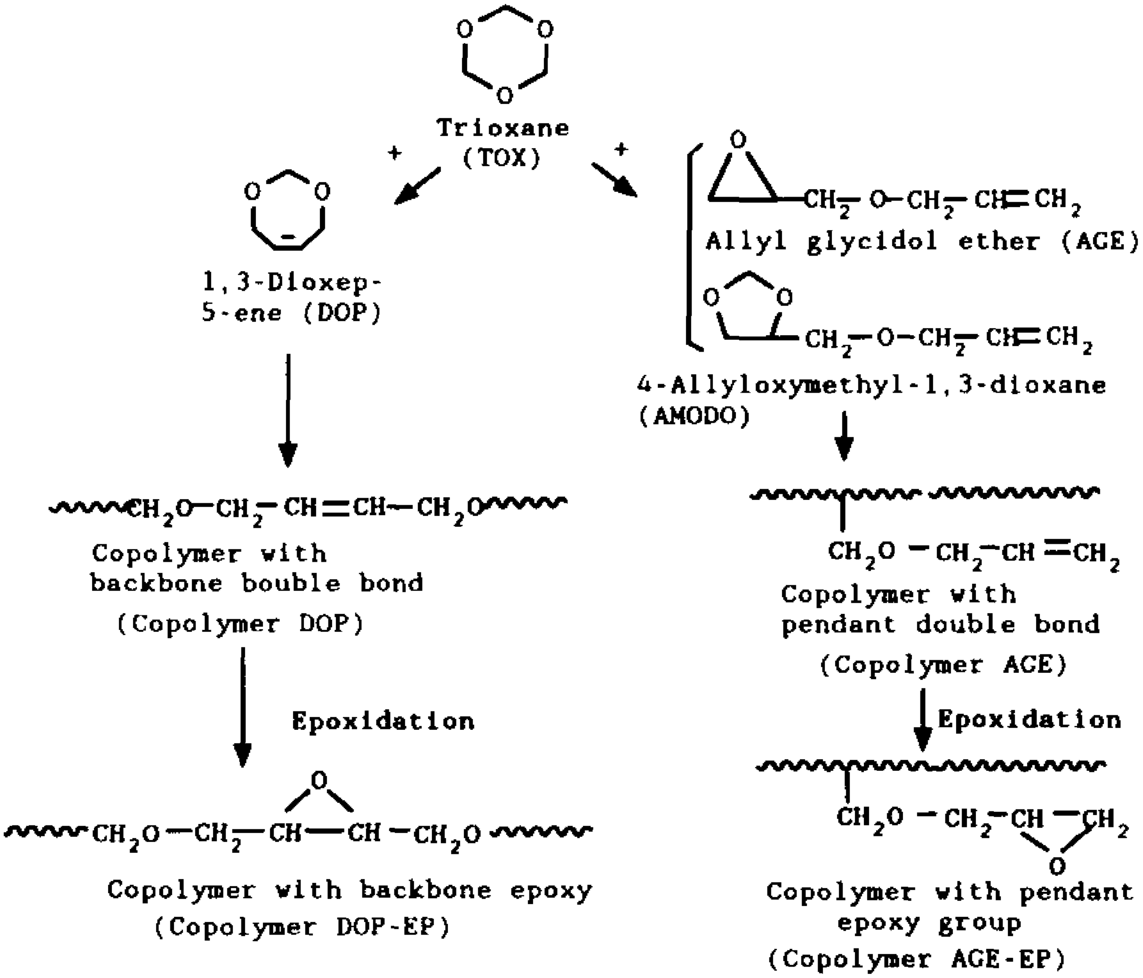
4. Acetal Copolymers with Backbone and Pendant Epoxy Functional Groups

4.1. Introduction

The epoxy group is very reactive toward a large number of functional groups, including acid, base and amines[1]. It can act as a potential acceptor of H^+ and free radical, which are severe degrading agents against polyacetal.

In this study, acetal copolymers carrying reactive backbone and pendant epoxy functionalities were synthesized. The copolymers with backbone epoxy groups were prepared by epoxidation of copolymers with backbone double bond.

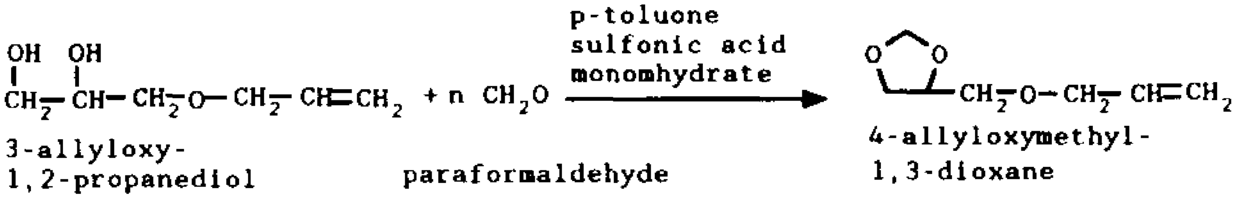
Acetal copolymers with pendant epoxy functionalities were prepared through epoxidation of copolymers of allyl glycidyl ether or 4-allyloxymethyl-1,3-dioxolane with trioxane. The reactivity of both types of epoxy group were investigated and compared. Both types of epoxy groups have been demonstrated to serve as active sites for further modifications, e.g. amination.


Trioxane
(TOX)
+
+
1,3-Dioxep-5-ene (DOP)
Allyl glycidol ether (AGE)
4-Allyloxymethyl-1,3-dioxane
(AMODO)
CH2–O–CH2–CH=CH2
Copolymer with
backbone bouble bond
(Copolymer DOP)
Copolymer with
pendant double bond
(Copolymer AGE)
Epoxidation
Epoxidation
Copolymer with backbone epoxy
(Copolymer DOP-EP)
Copolymer with pendant
epoxy group
(Copolymer AGE-EP)

4.2. Experimental

4.2.1. Synthesis of 1,3-dioxep-5-ene (DOP) and 4-allyloxymethyl-1,3-dioxolane (AOMDO)

The comonomer, 1,3-dioxep-5-ene (DOP) and 4-allyloxymethyl-1,3-dioxolane (AOMDO), were synthesized through an acid catalyzed reaction of cis-2-butene-1,4-diol and 3-allyloxy-1, 2-propanediol with paraformaldehyde respectively based on a reported procedure[2,3].



99 g (0.75 mol) of 3-allyloxy-1,2-propanediol, 22.5 g (0.75 mol) of paraformaldehyde, 0.3 g of p-toluene sulfonic acid monohydrate and 50 ml of toluene as solvent were placed in a 250 ml round bottom flask fitted with a Dean Stark trap. The mixture was refluxed at about 110°C until stoichiometric amount of water (12-13 ml) was collected in the trap. The crude product was distilled under the reduced pressure at 5-6 mm Hg. The distillate at 64-70°C was collected. 85 g of product was obtained with a yield of 79%.

Comonomer allyl glycidyl ether (AGE) used was from Aldrich Chemical Company, Inc.

4.2.2. Copolymerisation of trioxane with allyl glycidyl

ether and 4-allyloxymethyl-1,3-dioxolane (AOMDO)

A dry test tube (25x150mm) equipped with a magnetic stirrer was charged with 9 grams of trioxane. The tube was then capped with a serum stopper, purged with nitrogen and evacuated through a needle connecting the serum stopper to a vacuum pump. The desired amount of comonomers was injected into the tube through the serum stopper. The contents of tube were kept at 65°C in an oil bath. Then, the required amount of boron trifluoride etherate was injected through the serum stopper into the completely melted mixture under stirring. After addition of the initiator, the colorless mixture become a milky white solid within a few minutes. The polymerization was allowed to proceed at 65°C for 20 hrs. At the conclusion of the polymerization, the polymer was removed and pulverized in a blender. The crude polymer was then placed in 30 ml of methanol containing 1% of triethanolamine, TEA, stirred for 1 hr and then collected by filtration and dried. The typical yield was about 85%.

The unstable end groups of the copolymers were removed by solution base hydrolysis, following a procedure described before (Section 2.2.4.). The hydrolysis was also conducted heterogeneous in 2N NaOH aqueous solution described below: 5.2 g of copolymer (e.g. copolymer DOP) and 10 ml of 2N NaOH solution were placed in a 50 ml round bottom flask equipped with a air condenser and a magnetic stirrer. The contents were kept in an oil bath at the temperature range of 95-100°C under stirring for 8 hrs. The unstable end groups were removed by the strong base NaOH. The resulting copolymer was collected by filtration, and then washed with distilled water until the filtrate was neutral, and then further washed with acetone 3 times. Yield of copolymer after hydrolysis was 90.8%.

4.2.3. Copolymerization of trioxane with 1,3-dioxep-5-ene

Procedure for the copolymerization of trioxane with 1,3-dioxep-5-ene (copolymer DOP) has been reported[3].

4.2.4. Epoxidation of copolymers

Epoxides may be obtained in one step from alkenes by insertion of an oxygen atom into the π-bond. This can be accomplished through the use of certain organic derivatives of hydrogen peroxide known as peracids[4]. They contain a weak oxygen-oxygen bond and serve as oxygen atom transfer reagents. The reaction of cis-alkenes gives rise to cis-epoxides and that of trans-alkenes to trans-epoxides[5].

A 100 ml of round bottle flask was charged with 2.0 g of copolymer DOP (sample 137A, 4.27 mol% of double bond). The flask was capped with a serum stopper and evacuated at 120°C through a needle connecting the serum stopper to a vacuum pump for 1 hour to remove moisture in copolymer. The flask was purged thoroughly with dry nitrogen gas 4 times intermittently during evacuation. The system was then cooled to room temperature. The serum stopper was removed briefly for the addition of 3-chloroperoxybenzoic acid and recapped immediately. Then the flask was evacuated and purged again with dry nitrogen as above at room temperature for 30 minutes. The flask was filled with 10 ml of methylene chloride through a syringe under dry nitrogen gas pressure. The epoxidation reaction was carried out in an ice bath for 6 hours and then continued at room temperature overnight. The reaction mixture was filtered and washed with acetone 3 times to remove the acid by product and unreactive peracid. 1.93g of dry epoxidized copolymer was collected.

The same procedures were used for epoxidation of copolymer with pendant double bond.

4.2.5. Graft of epoxidised copolymers

A test tube was charged with 0.20 g of epoxidized copolymer TOX-DOP or copolymer TOX-AGE and 0.20 g of phenethylamine in 1 ml of toluene as solvent. The reaction was conducted in a 100°C oil bath for different reaction times from 0.5 to 24 hours. The reaction mixture was then cooled to room temperature. After removing the unreacted amine and solvent by filtration, the solid was washed with acetone 3 times. The reactivity of two types of epoxy group was compared under the same reaction conditions.

Different amines, such as secondary amine, N-benzylmethyl amine, and a long chain monoamine terminated polypropylene oxide (MW 600, from Scientific Polymer Products, Inc.) were used to react with epoxy copolymer at similar reaction conditions.

4.2.6. Thermal stability of copolymers

TGA thermograms were obtained under nitrogen purging at the rate of 50 ml/min.. The heating rate is 10 °C/min from room temperature to 300°C, with sample mass of 2-4 mg. The TGA analyzer used is DuPont 990.

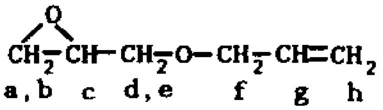
4.2.7. NMR analysis

All NMR spectra were obtained on an IBM 200-SY NMR spectrometer operated at 200 MHz for ^1H using Bruker software. The chemical shifts were referenced to tetramethylsilane at 0 ppm for ^1H spectra and DMSO-d_6 at 39.5 ppm for ^{13}C spectra. Hexafluoroisopropanol (HFIP) was used as solvent for ^{13}C spectra at 45 °C. A Distortionless enhanced polarization transfer (DEPT) ^{13}C spectrum was obtained to identify the CH and CH_2 groups using a DEPT program from Bruker software. In solvent HFIP, the 90° pulse width was determined as 15.2 μs for ^1H and 12.0 μs for ^{13}C.

4.3. Results and Discussion

4.3.1. Structural information of allyl glycidyl ether (AGE) and 4-allyloxymethyl-1,3-dioxolane (AOMDO)

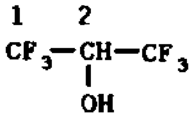
Fig. 4-1 shows a ^1H NMR spectrum of comonomer allyl glycidyl ether (AGE) in DMSO-d_6 at room temperature.



AGE

The two quartets at 2.55 and 2.76 ppm are due to protons **a** and **b** coupled with proton **c**. A sharp singlet at 3.36 ppm is due to water in the solvent. A multiplet at 3.12 ppm is due to proton **c** coupled with protons **a**,**b** and **d**,**e**. Protons **d**,**e** also couple with proton **c** to give two quartet at 3.25 and 3.70 ppm. A multiplet at 5.8-6.0 ppm is due to proton **g** on the double bond; the multiplet at 5.10-5.35 ppm, due to two protons **h** in different magnetic environment. Protons **f** couple with proton **g**, leading to a doublet at 4.0 ppm.

Fig.4-2 (a) shows a DEPT ^{13}C spectrum of AGE in hexafluoro- isopropanol (HFIP) at 45 °C.



$$\overset{1}{CF_3}-\overset{2}{\underset{OH}{CH}}-CF_3$$

HFIP

The parameters were set to produce a 135° pulse to observe

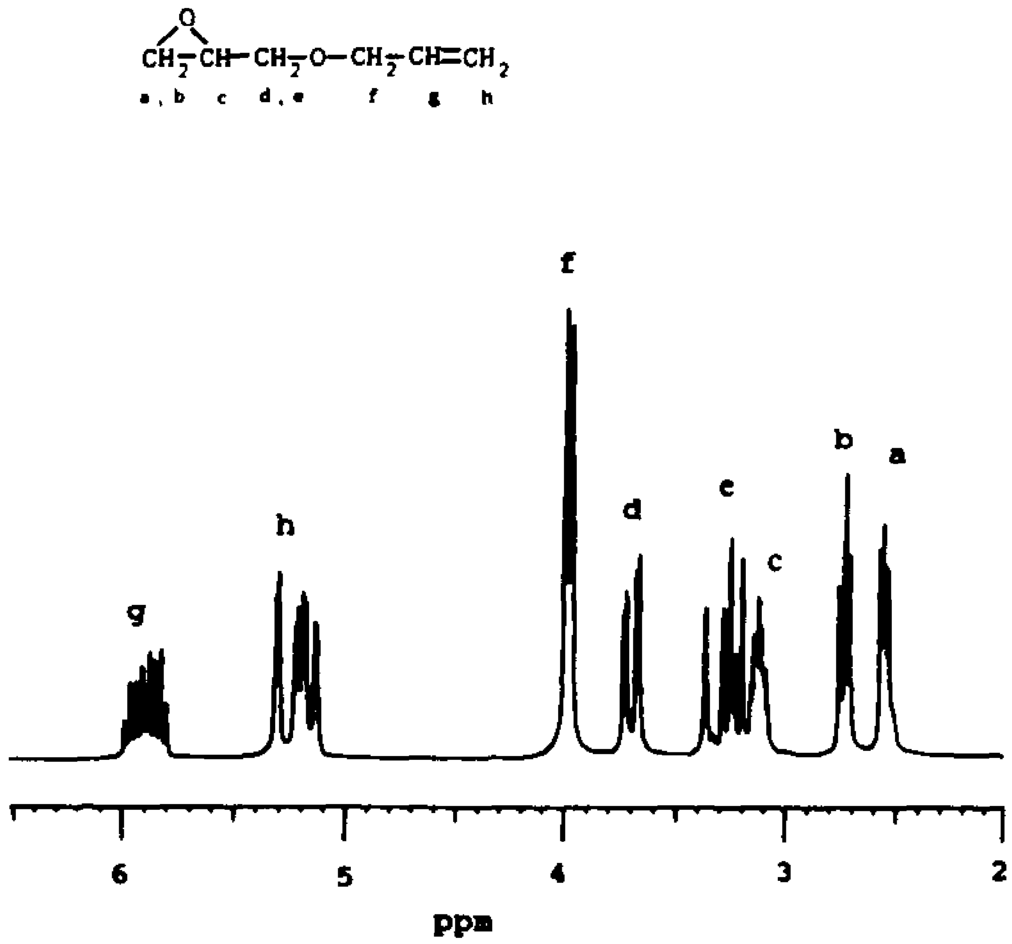


Fig. 4-1 ^1H NMR spectrum and assignment of comonomer allyl glycidyl ether (AGE) in DMSO-d_6 at room temperature.

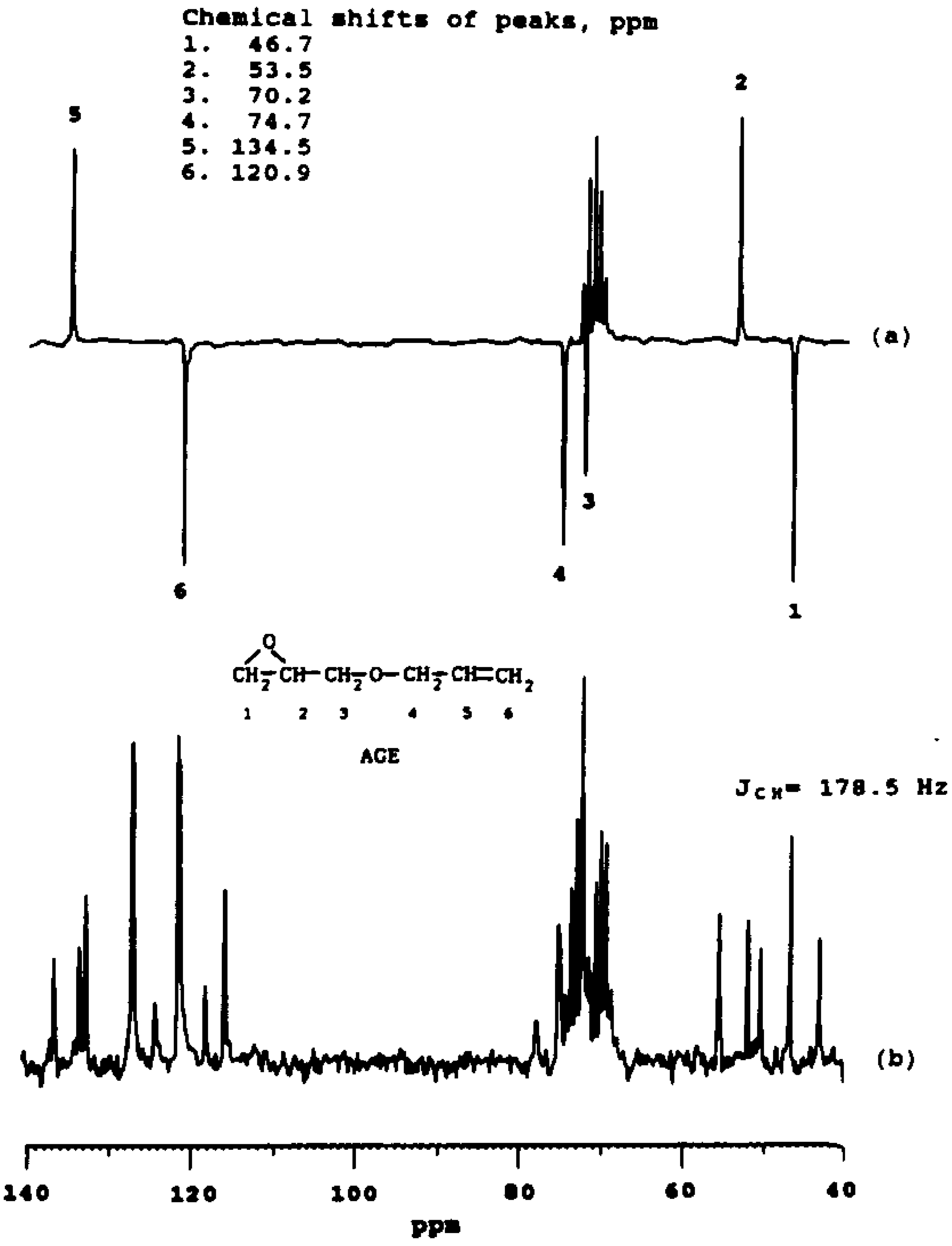
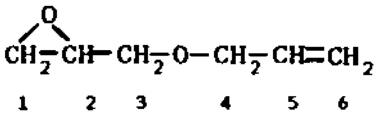


Fig. 4-2 DEPT ^{13}C spectrum of comonomer AGE in HFIP at 45°C.

the CH_2 and CH. The absorptions due to carbon of CF_3, having no hydrogen attached, was conveniently missing. Carbon **2**, coupled with one hydrogen which in term interacts with six ^{19}F, leads to a heptet centered at 72.8 ppm. Fig.4-1 (b) is a coupled ^{13}C spectrum, giving a value of 178.5 Hz for J_{CH}. Thus, D2 in DEPT program was set to 0.0028, i.e. $0.5/J_{CH}$. Four negative peaks in the DEPT spectrum are due to methylene groups.

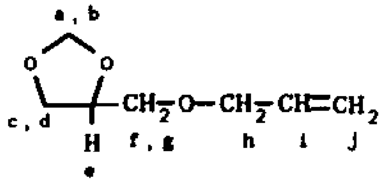


AGE

The peak at 120.9 ppm is assigned to carbon **6** of double bond. The peak at 46.7 ppm is due to carbon **1** of epoxy group. Peaks at 70.2 and 74.7 ppm are due to carbon **3** and **4** respectively. Two positive peaks at 53.5 and 134.5 ppm are assigned to carbons **2** and **5** respectively.

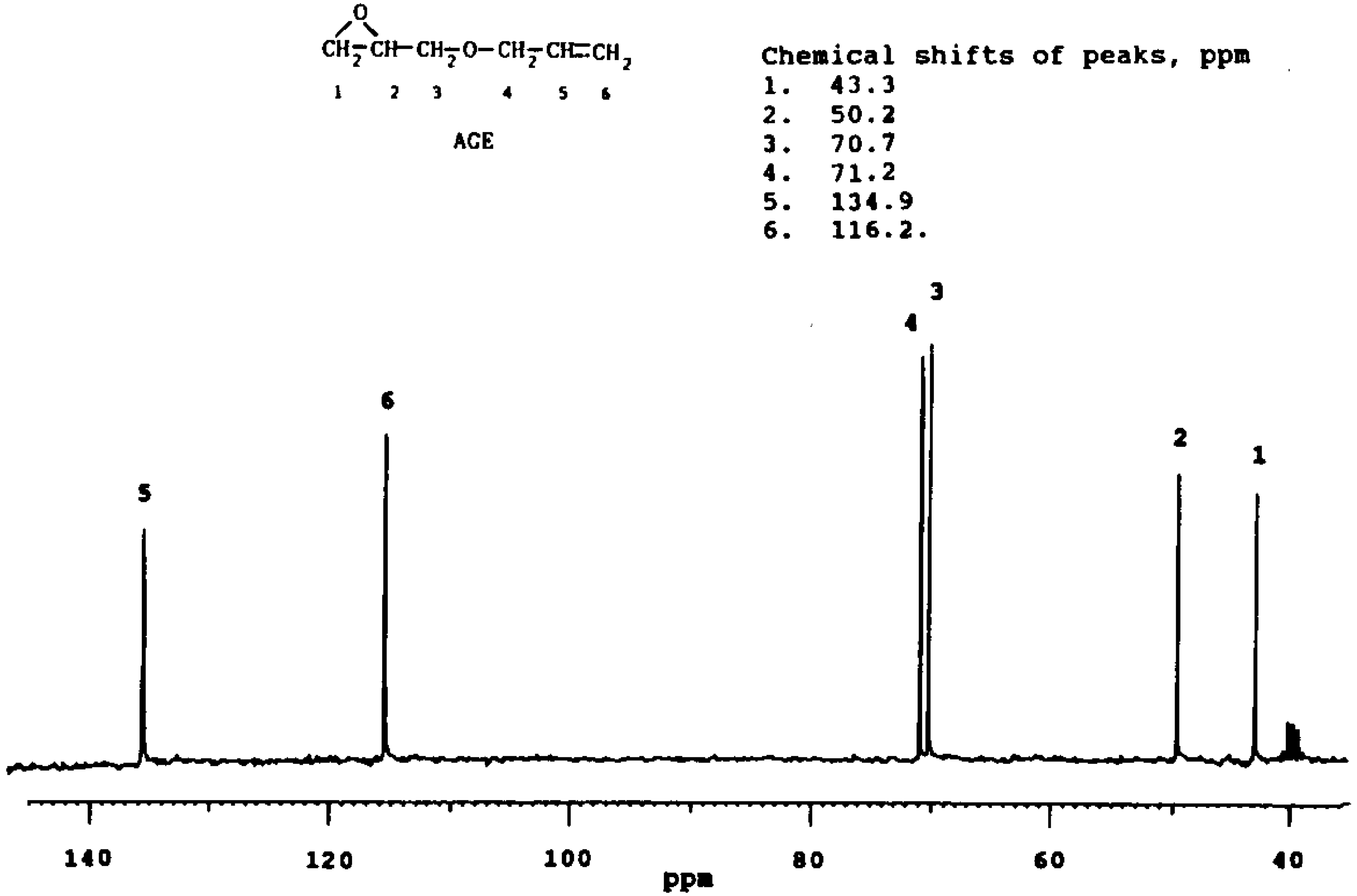
Fig. 4-3 shows a ^{13}C spectrum of AGE in DMSO-d_6 at 120 °C. This is used to assign the ^{13}C spectrum of copolymers.

Fig. 4-4 is ^1H NMR spectrum of comonomer 4-allyloxymethyl-1,3-dioxolane in DMSO-d_6 at room temperature.



AOMDO

^1H NMR structural data of monomer 1,3-dioxep-5-ene have been documented[2].



Chemical shifts of peaks, ppm
1. 43.3
2. 50.2
3. 70.7
4. 71.2
5. 134.9
6. 116.2.

Fig. 4-3 ^{13}C spectrum of comonomer AGE in DMSO-d_6 at 120°C.

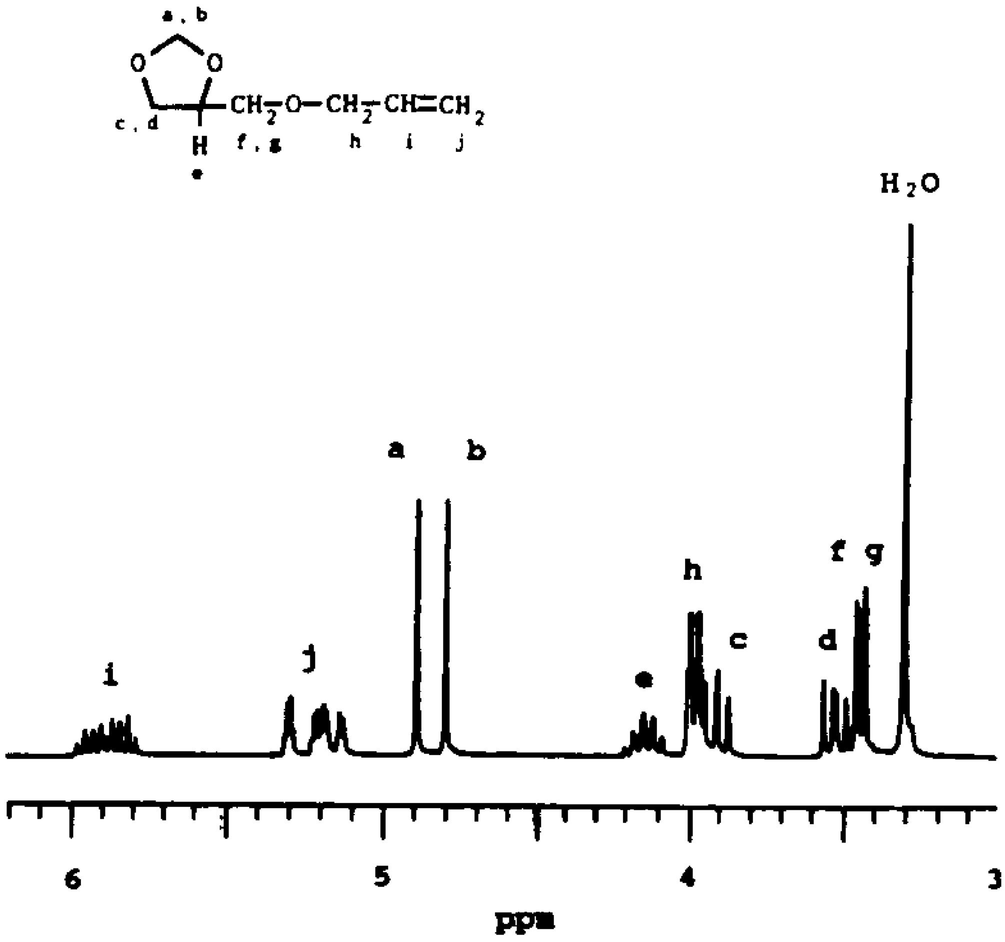
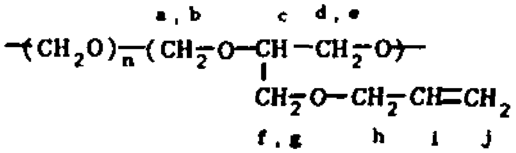


Fig. 4-4 ^{1}H NMR spectrum and assignment of comonomer 4-allyloxymethyl-1,3-dioxalane (AOMDO) in DMSO-d_6 at room temperature.

4.3.2. Copolymers of trioxane with allyl glycidyl ether (AGE) and allyloxymethy-1,3-dioxalane (AOMDO)

The structure of copolymers TOX with AGE (copolymer AGE) and AOMDO (copolymer AOMDO) is identical.



$$-(CH_2O)_n-(CH_2-O-\underset{CH_2-O-CH_2-CH=CH_2}{CH}-CH_2-O)-$$

Copolymer AGE or
Copolymer AOMDO

Fig. 4-5 shows a ^1H NMR spectrum of copolymer TOX-AGE in DMSO-d_6 at 120 °C. The multiplet at 2.47 ppm is due to proton impurity of DMSO-d_6 and a broad peak at 2.70 ppm is due to water in the solvent. The multiplets at 5.8~6.0 ppm and 5.0~5.3 ppm are due to protons **i** and **j** on the double bond. A doublet at 3.9~4.0 ppm is due to the protons **h** of methylene group. Two overlapping multiplets at 3.4~3.8 ppm are due to protons **d,e** and **f,g** of methylene groups. A multiplet at 3.85 ppm is due to the proton **c** of methine group. The main peak **M** at 4.84 ppm is due to protons from $-(CH_2O)_n-$. The incorporation of comonomer AOMDO or AGE based on formaldehyde can be calculated from integral of the multiplet of proton **i** and the main peak **M** based on the equation:

$$\text{Incorp. (mole\%)} = \frac{\text{Area of peak i}}{\text{Area of peak (i + M/2)}} \times 100\%$$

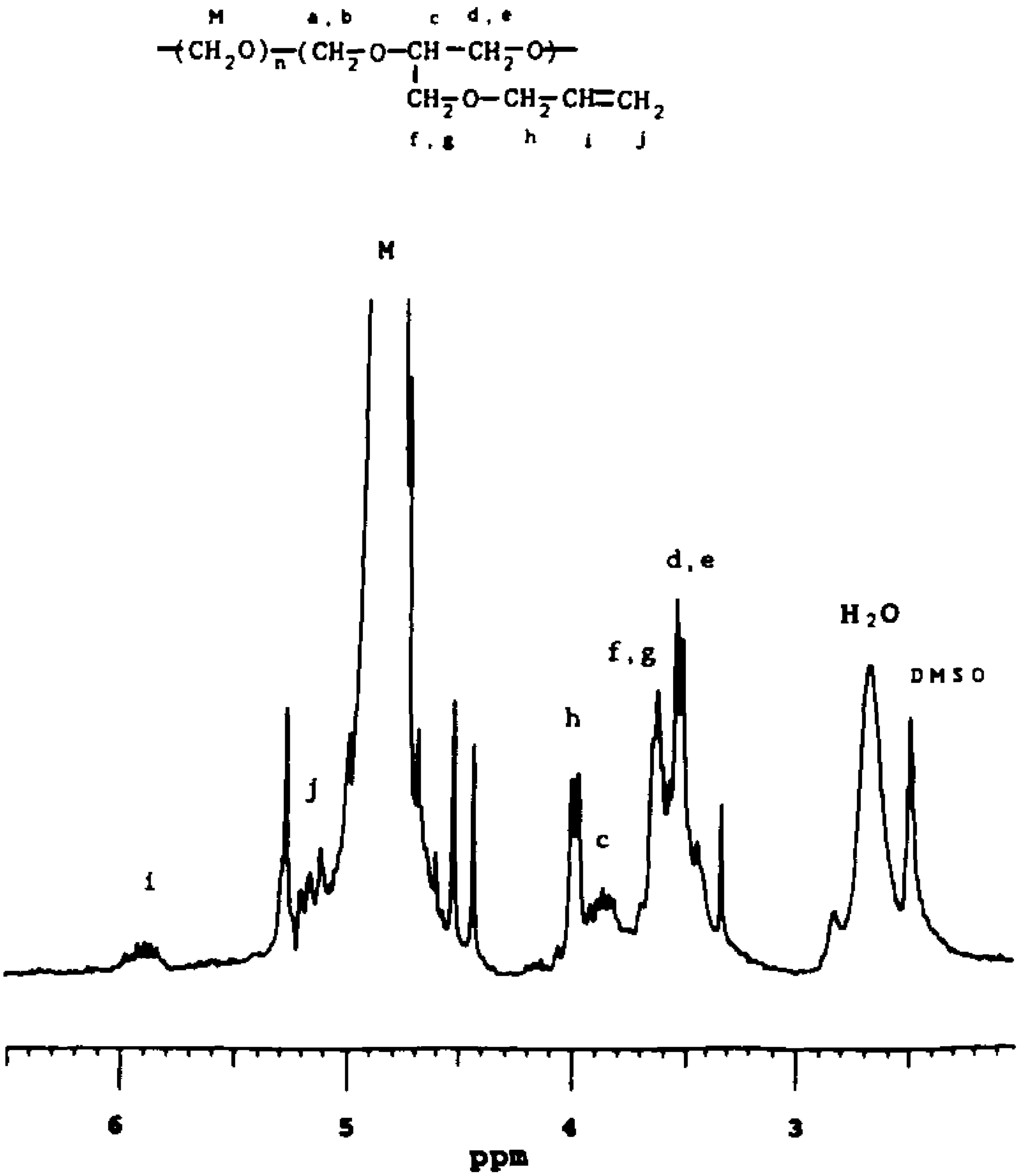


Fig. 4-5 ^{1}H NMR spectrum and assignment of copolymer AGE in DMSO-d_6 at 120°C.

Table 4-1 presents the results of copolymerization of TOX with AOMDO. The feed of comonomer AOMDO was calculated based on trioxane ($C_3H_6O_3$), but the mole % incorporation of comonomer was calculated based on formaldehyde units (CH_2O). As the feed of AOMDO increased, the incorporation increased. However the yield of base hydrolysis increased to a maximum (60 %) and then decreased. Table 4-2 summaries the data for the copolymerization of TOX with AGE. The incorporation of AGE is higher than that of AOMDO at comparable levels of feed. Thus, the 3-member ring comonomer AGE is more reactive, as expected in ring opening polymerization, than the 5-member ring comonomer AOMDO.

Fig. 4-6 shows TGA thermograms of copolymer AGE and AOMDO. No degradation of the copolymer took place at temperature lower than 220 °C.

Table 4-1 Copolymerization of trioxane with 4-allyloxymethyl-1,3-dioxolane

Sample number	Comonomers				$BF_3 \cdot Et_2O$	Copolymer			
	TOX		AOMDO			Feed	Incorp	Yield	Yield'
	g	mmol	g	mmol	μl	mol%	mol%	w%	w%
53A	9.5	105.6	0.5	3.5	8	3.2	0.38	95	38.1
53B	9.0	100.0	1.0	6.9	8	6.5	0.67	89	50.6
53C	8.5	94.4	1.5	10.4	8	9.9	0.82	89	56.3
75A	8.0	88.9	2.0	13.9	16	13.5	1.01	89	60.0
75B	7.5	83.3	2.5	17.4	24	17.3	1.07	68	54.0
75C	7.0	77.8	3.0	20.8	32	21.1	1.26	66	54.7

Yield: Copolymer washed with 1% TEA methanol solution
Yield': From base hydrolysis
Feed: Based on trioxane, $C_3H_6O_3$
Incrop.: Based on formaldehyde, CH_2O

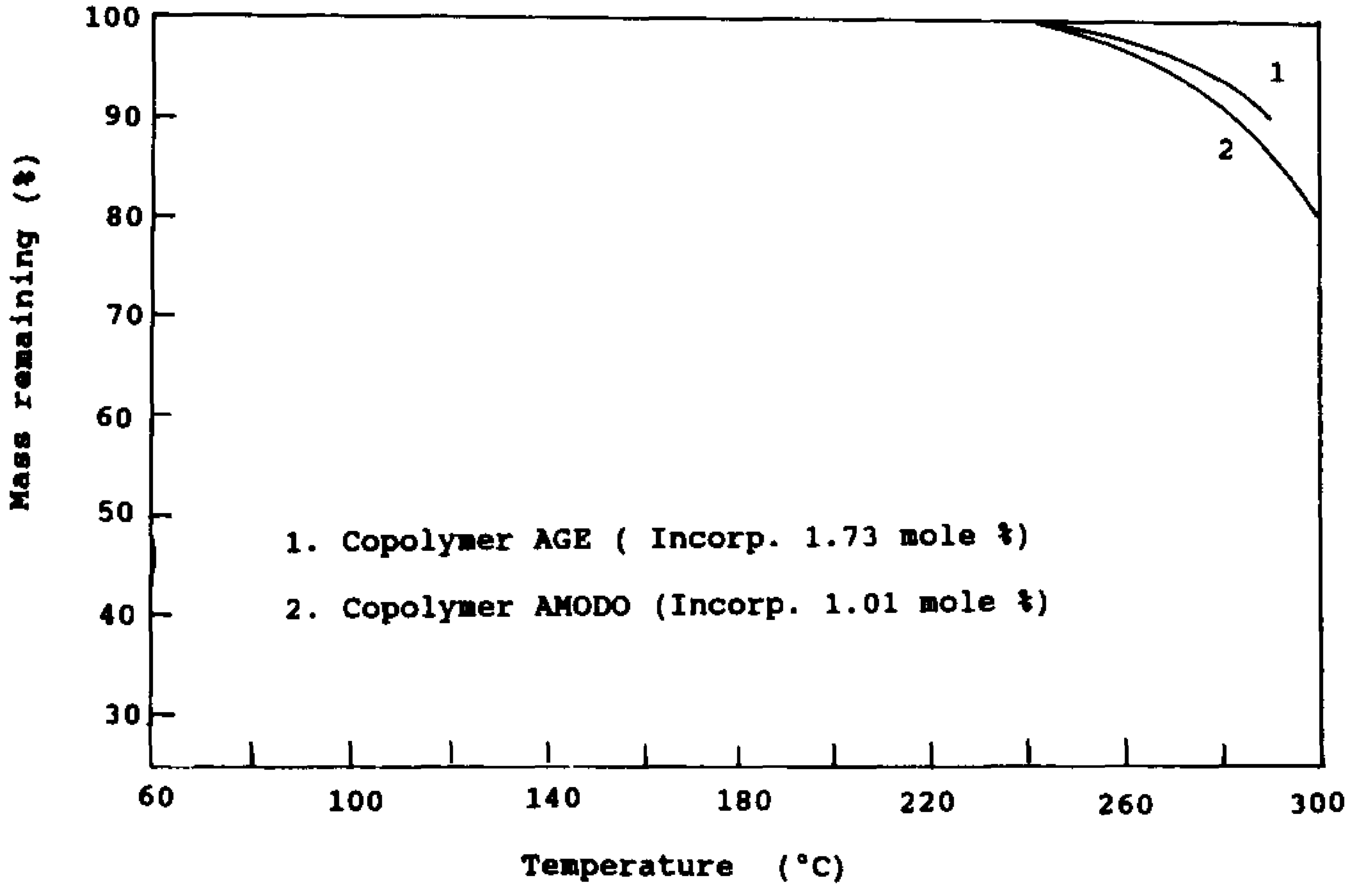


Fig. 4-6 TGA thermogram of copolymers AGE and AOMDO.

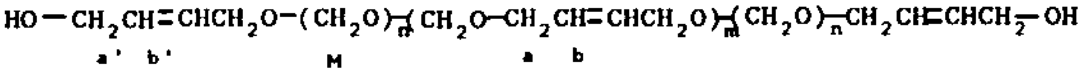
Table 4-2 Copolymerization of trioxane with Allyl glycidyl ether

Sample number	Comonomers				$BF_3 \cdot Et_2O$	Copolymer			
	TOX		AGE			Feed	Incorp	Yield	Yield'
	g	mmol	g	mmol	µl	mol%	mol%	w%	w%
40	9.0	100.0	1.0	8.8	18	8.09	1.73	87.0	63.3
92A	8.5	94.4	1.5	13.2	32	12.3	2.52	88.3	61.0
92B	8.0	88.9	2.0	17.5	24	14.5	3.24	75.3	66.0
92C	7.5	83.3	2.5	21.9	28	20.8	3.81	65.7	70.0

Yield: Copolymer washed with 1% TEA methanol solution
Yield': From base hydrolysis
Feed: Based on trioxane, $C_3H_6O_3$
Incorp.: Based on formaldehyde, CH_2O

4.3.3. Copolymer of trioxane with 1,3-dioxep-5-ene

The structures of copolymer DOP has been established[2].



$$\underset{a'}{HO-CH_2}\underset{b'}{CH}=CHCH_2O-\underset{M}{(CH_2O)_n}(CH_2O-\underset{a}{CH_2}\underset{b}{CH}=CHCH_2O)_m(CH_2O)_n CH_2CH=CHCH_2-OH$$

Copolymer DOP

Fig. 4-7 shows a ^1H NMR spectrum of the copolymer hydrolyzed heterogeneously from 2 N NaOH solution. It is the same as the copolymer from solution base hydrolysis. A triplet at 5.72 ppm is due to the proton **b** of methine group from comonomer unit. A doublet at 4.2 ppm is due to the protons **a** of methylene group next to the methine. The incorporation of comonomer is 6.82 mol % based on formaldehyde for the feed of 3/7 (DOP/TOX) by weight calculated from the ^1H NMR spectrum:

$$\text{Incorp. mol\%} = \frac{\text{Area of peak } (a+b)/3}{\text{Area of peak } [(a+b)/3 + M]}$$

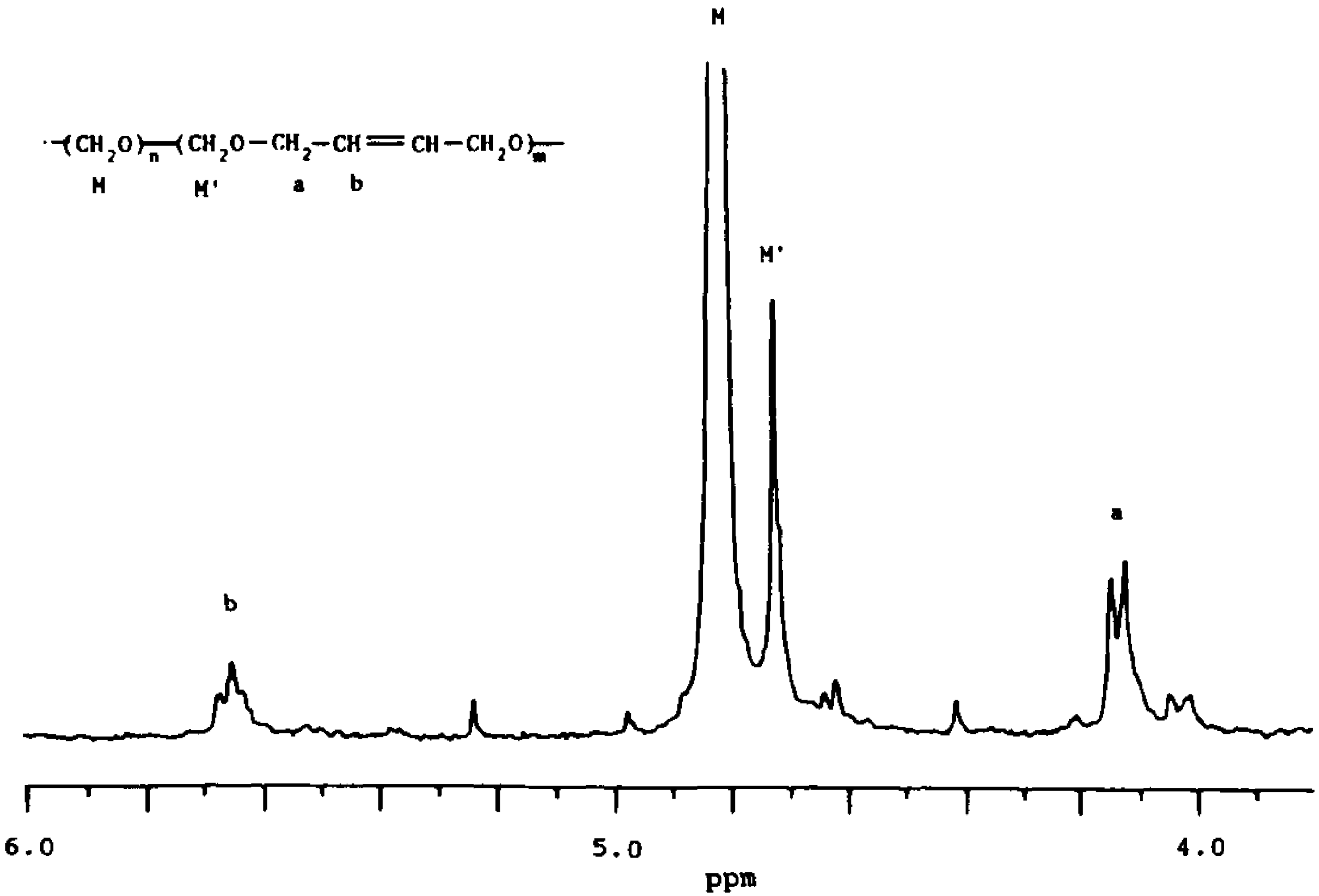
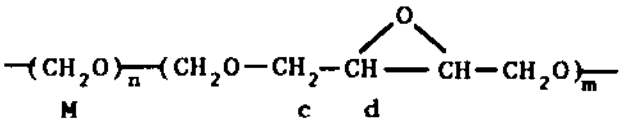


Fig. 4-7 ^1H NMR spectrum of copolymer DOP hydrolyzed in 2N NaOH aqueous solution.

Fig.4-8 shows TGA curves of copolymer obtained from sodium hydroxide suspension and TEA-BA-DMF homogeneous system. Both copolymers are stable, no weight loss was observed before 220 °C. This further confirms the efficient end group hydrolysis of copolymer from both processes.

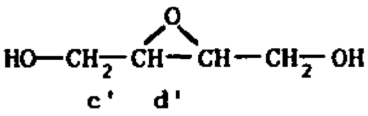
4.3.4. Epoxidation of copolymers

Copolymers DOP after hydrolysis were epoxidized to form copolymers with backbone epoxy groups:



Copolymer DOP-EP

Fig. 4-9 shows a ^{1}H NMR spectrum of such a copolymer. A multiplet at 3.5-3.9 ppm is due to the protons **c** of methylene group; a triplet at 3.15 ppm, due to the methine **d**. This assignment is further confirmed by ^{1}H NMR spectra of a model compound,



where **c′** absorbs at 3.58 ppm, **d′** at 3.03 ppm. Two small peaks, doublet **a** and triplet **b** are from the unreacted DOP units, as shown in the copolymer DOP spectrum (Fig. 4-7). The conversion of double bond to epoxy can be calculated from the ^{1}H NMR spectrum using the equation below:

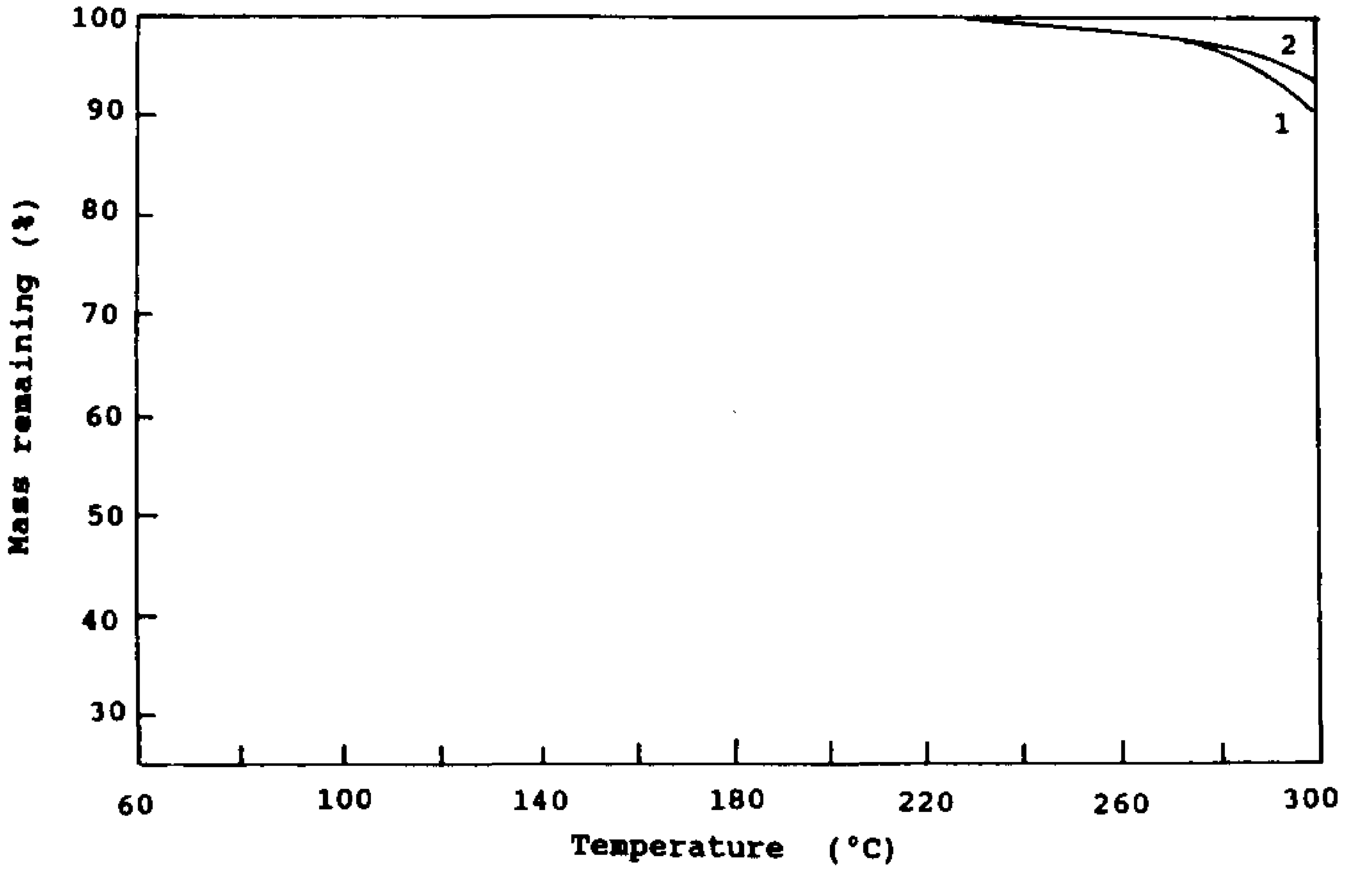


Fig. 4-8 TGA thermogram of copolymer DOP hydrolyzed in 2N NaOH aqueous solution (1) and dimethylformamide-benzyl alcohol containing 1% TEA solution (2).

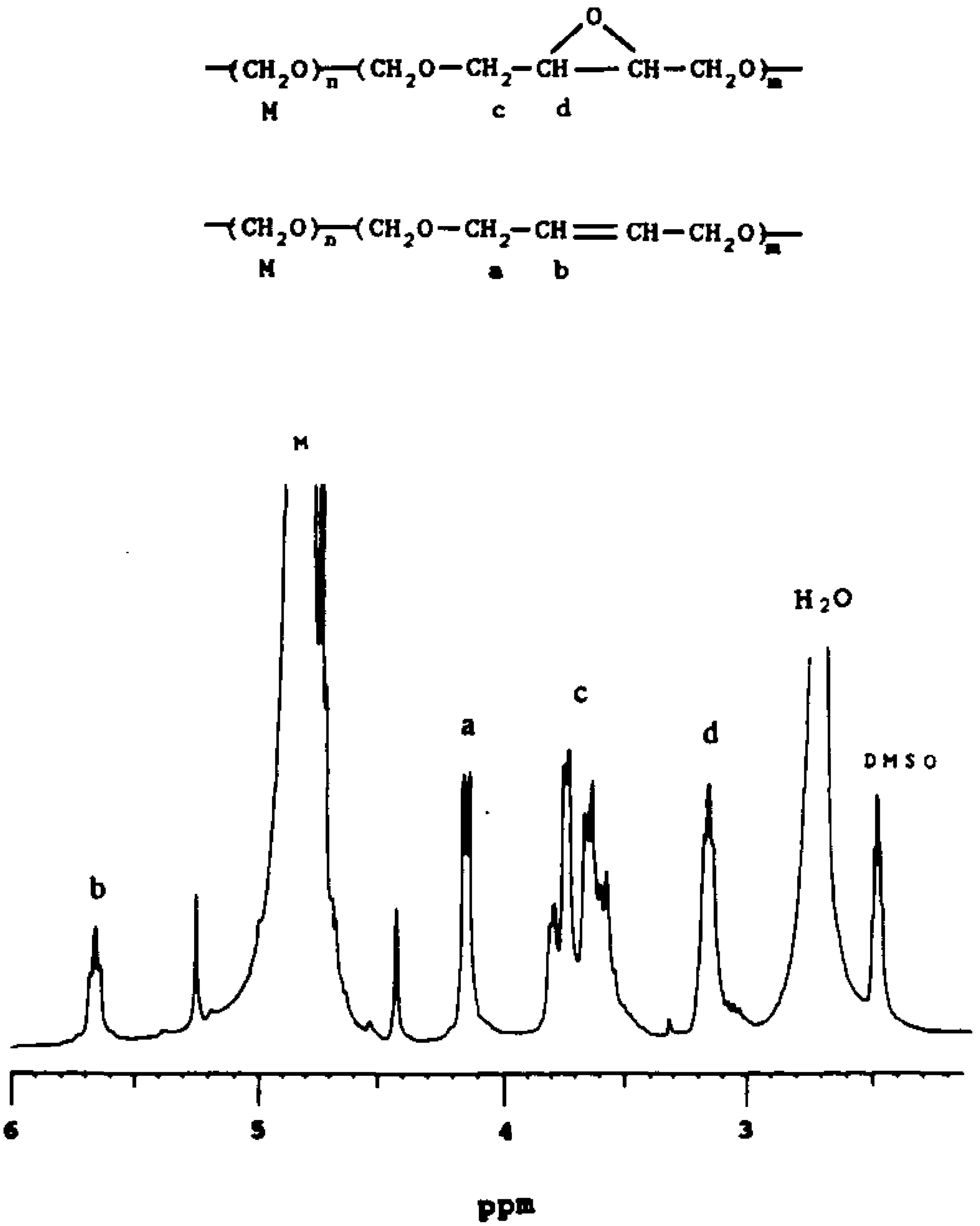


Fig. 4-9 ^1H NMR spectrum of copolymer DOP-EP in DMSO-d_6 at 120°C.

$$\text{Conversion}(\%) = \frac{\text{Area of Peak c}}{\text{Area of Peak (c + a)}}$$

$$\text{or} = \frac{\text{Area of Peak d}}{\text{Area of Peak (b + d)}}$$

For this sample, 80.1% of double bond was converted to epoxy, i.e. 5.46 mole% of epoxy groups in the copolymer. Table 4-3 summaries the conversion of double bonds to epoxy groups. About 70-80% of double bond was converted to epoxy group.

Table 4-3 Epoxidation of Copolymers with backbone and pendant double bond

Sample Number	Double bond Content mole%	Conversion of Epoxidation (%)	Polymer type
197	6.81	80.1	Backbone double bond
137A	4.27	71.4	
134A	4.27	74.9	
131A	4.27	72.4	
128	4.27	76.5	
125	4.27	74.5	
142	3.54	87.7	Pendant double bond
137B	3.16	100.0	
134B	3.16	84.9	
131B	3.16	76.8	
130	3.16	81.4	

Reaction conditions: bouble bond/peracid = 1, 0-5°C, 6 hrs, under N_2.

Fig. 4-10 shows a ^{13}C NMR spectrum of the same epoxidized copolymer DOP. The main peak at 89.9 ppm is due to the carbon of $(CH_2O)_n$; the peak at 128.3 ppm, due to carbon of CH of the double bond; the peak at 62.9 ppm, due to carbon of CH_2 next to the double bond. The peaks at 53.2

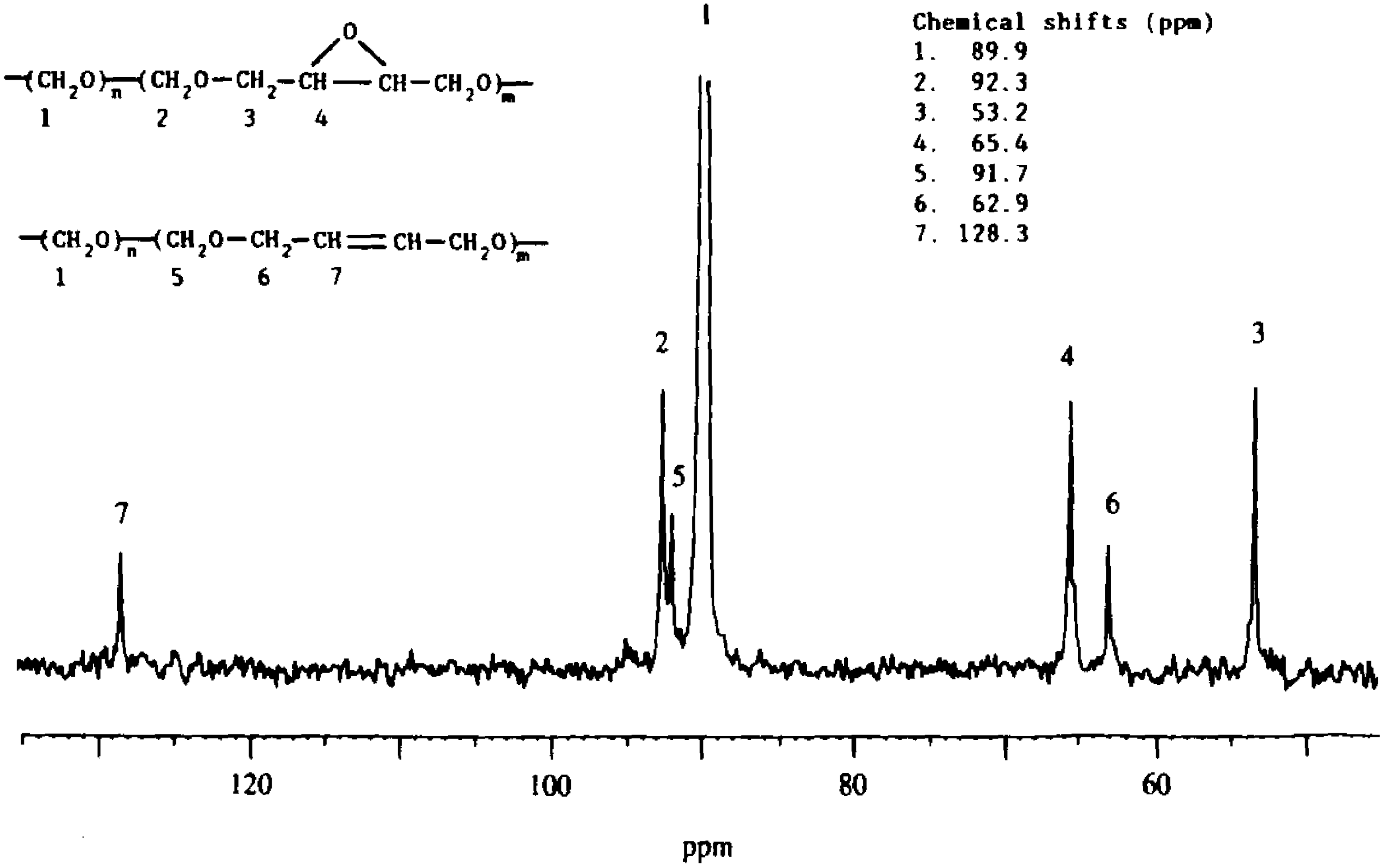
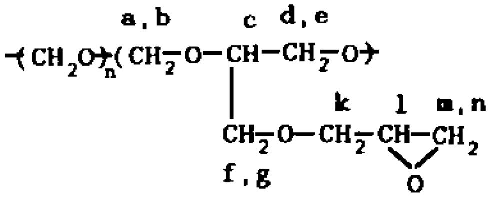


Fig. 4-10 ^{13}C spectrum of copolymer DOP-EP in DMSO-d_6 at 120°C.

and 65.4 ppm are due to carbons of epoxy group and carbons of CH_2 next to the epoxy group respectively. The peaks at 91.7 an 92.3 ppm are due to the CH_2O in the double bond unit and epoxy unit. If the epoxy groups were converted to diol, there should be an absorption at 70.7 ppm[6]. Thus it is clear that the epoxy groups were not converted to diols.

To obtain copolymers with pendant epoxy group (Copolymer AGE-EP), copolymer AGE was epoxidized:



Copolymer AGE-EP

Fig. 4-11 shows a typical ^1H NMR spectrum of epoxidized copolymer TOX-AGE. The multiplet at 5.8-6.4 and 5.1-5.4 ppm are due to the protons **i** and **j** of the unconverted double bond (see Fig. 4-5). A new peak at 3.0-3.1 ppm due to proton **l** on the epoxy group appears. Absorptions of protons **m** and **n** of methylene group at 2.50 and 2.70 ppm partially overlap with the peaks of DMSO-d_6 and water. Absorption of other protons **c**, **d**, **e**, **f**, **g**, and **k** from the two comonomer units, one with double bond and one with epoxy group overlap in the region 3.30-4.00 ppm. The conversion of double bonds to epoxy groups can be calculated from the ^1H absorptions of **l** and **i**:

$$\text{Conversion}(\%) = \frac{\text{Area of Peak l}}{\text{Area of Peak (i + l)}}$$

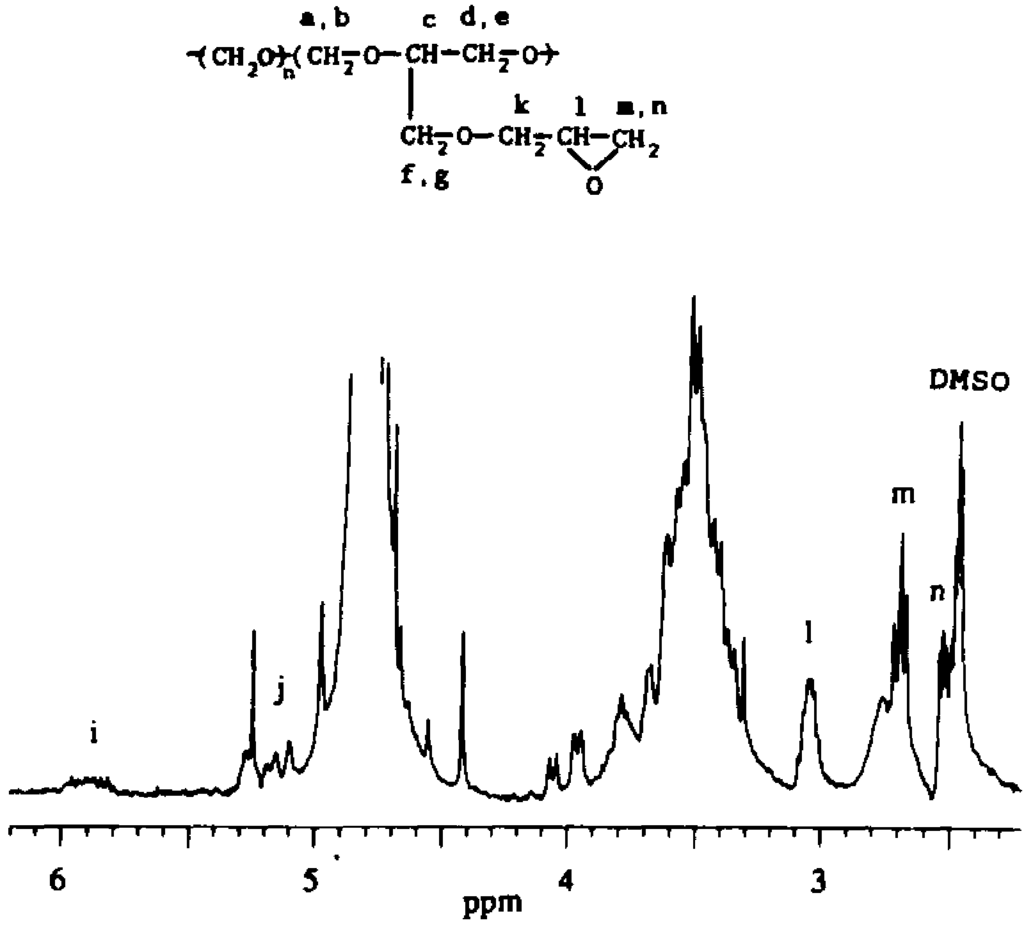
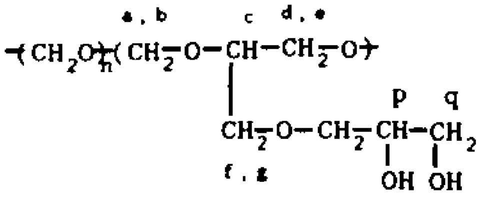


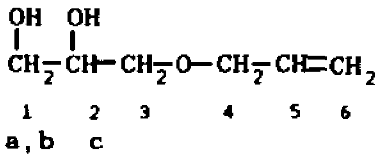
Fig. 4-11 ^{1}H NMR spectrum of epoxidized copolymer AGE in DMSO-d_6 at 120°C.

It is possible that some of epoxy groups may be converted to diol as depicted below:



$-(CH_2O)_n-(CH_2-O-CH(CH_2-O-CH_2-CH(OH)-CH_2OH)-CH_2-O)-$

For the assignment of the chemical shift of the diol, ^1H and ^{13}C NMR spectra of a model diol compound were determined in DMSO-d_6 at 120°C as well as in HFIP at 45°C:



$HOCH_2-CH(OH)-CH_2-O-CH_2-CH=CH_2$

The chemical shift of the protons, **a**, **b**, **c**, attached to carbon **1** and **2** are in the range 3.2-3.6 ppm as shown on Fig. 4-12. Thus, the chemical shifts of protons **p** and **q** in copolymer should be also in the range 3.2-4.0 ppm, where absorptions due to protons attached to the backbone dominate. On the other hand, ^{13}C NMR spectra are better resolved. The chemical shifts of carbons **1** and **2** of the model compound are at the 63.6 and 71.3 ppm respectively in DMSO-d_6 at 120°C (Fig. 4-13) or 67.2 and 74.7 ppm in HFIP at 45 °C (Fig. 4-14). Fig. 4-15 is a ^{13}C NMR spectrum of a copolymer AGE-EP in DMSO-d_6 at 120 °C. The peaks at 42.8 and 49.5 ppm indicate the presence of epoxy groups. But the

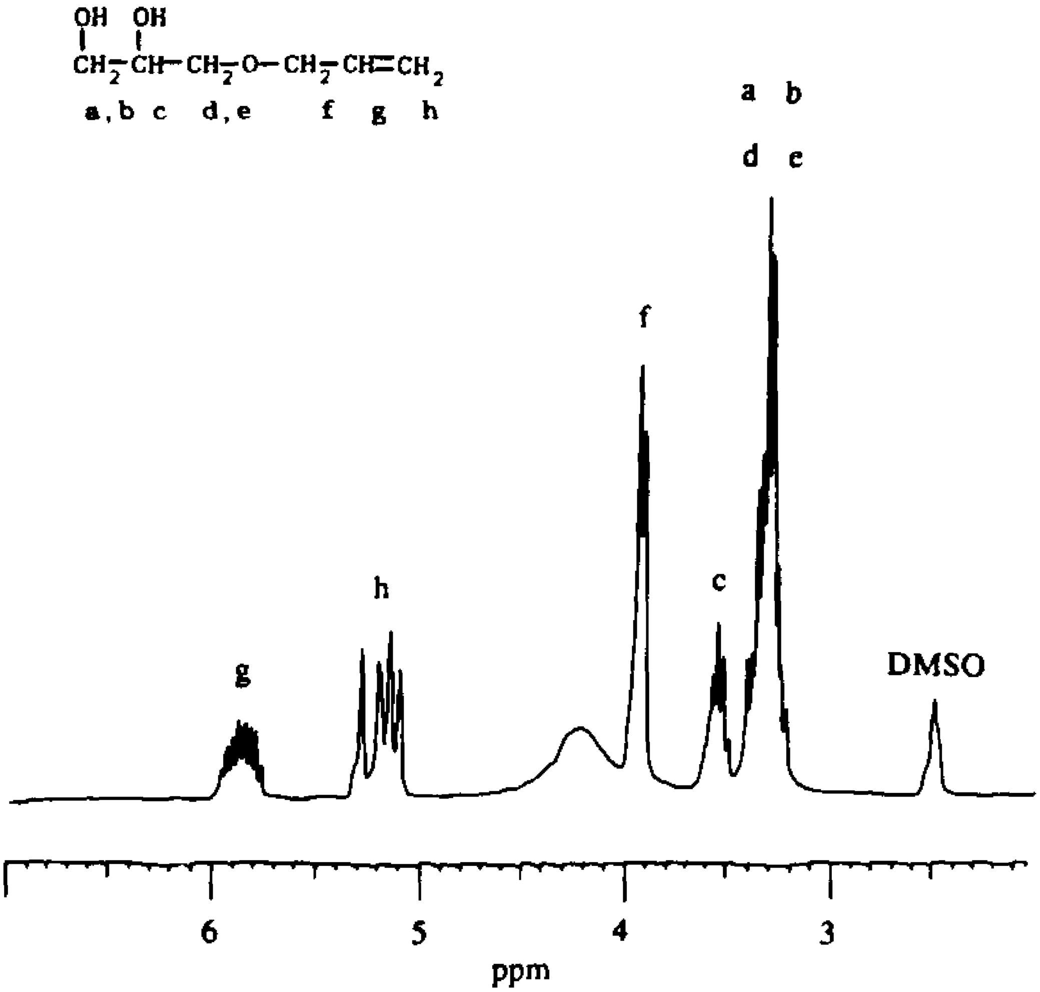
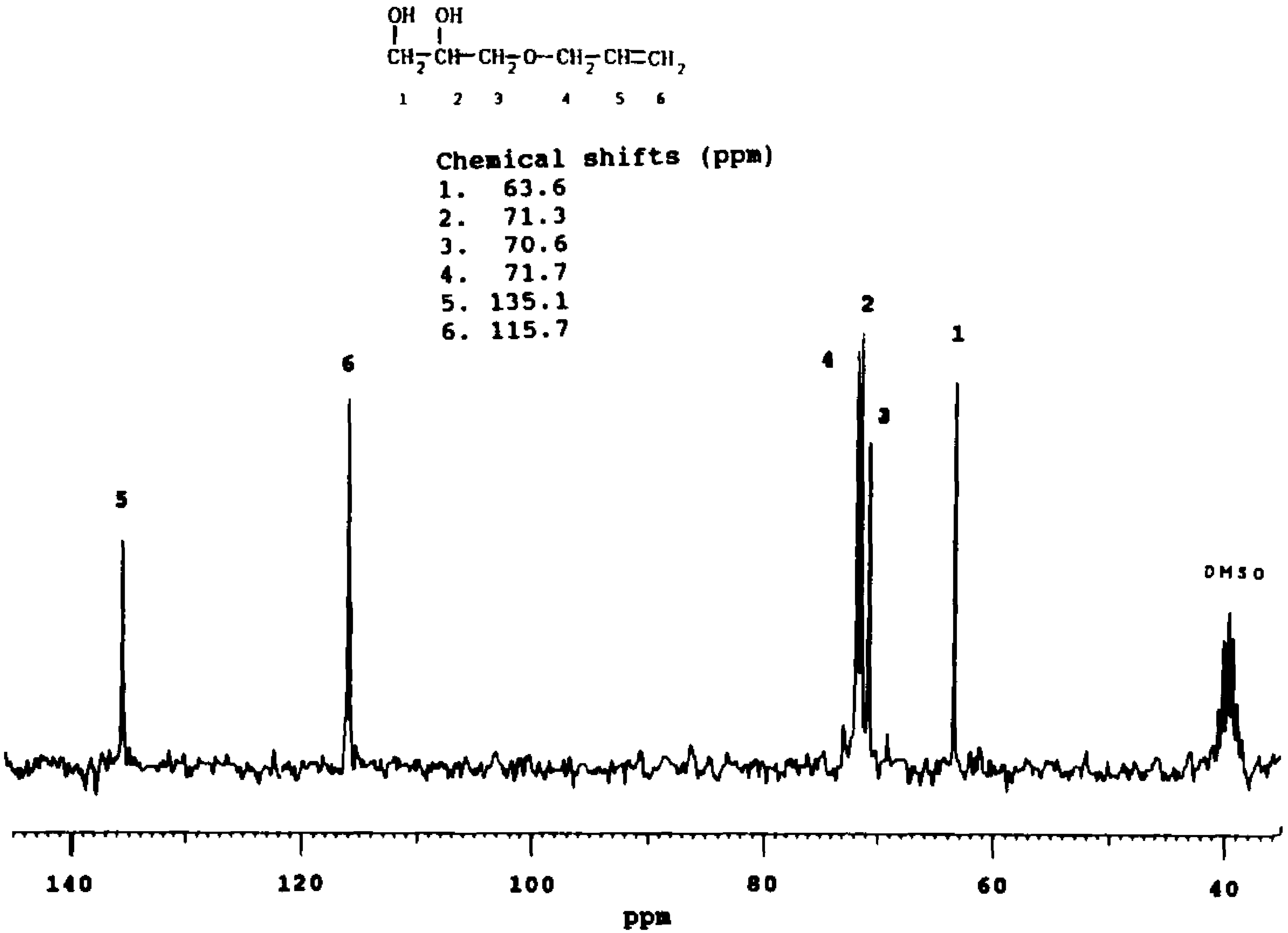


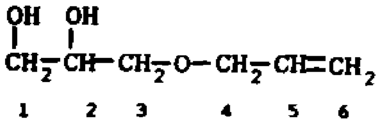
Fig. 4-12 ^{1}H NMR spectrum of model compound


$\mathrm{\overset{OH}{\underset{1}{C}H_2}-\overset{OH}{\underset{2}{C}H}-\underset{3}{C}H_2-O-\underset{4}{C}H_2-\underset{5}{C}H=\underset{6}{C}H_2}$

Chemical shifts (ppm)
1. 63.6
2. 71.3
3. 70.6
4. 71.7
5. 135.1
6. 115.7

Fig. 4-13 ^{13}C spectrum of model compound in DMSO-d_6 at 120°C.

Chemical shifts (ppm)
1. 67.2
2. 74.7
3. 74.5
4. 75.6
5. 137.1
6. 121.2



$CH_2(OH)-CH(OH)-CH_2-O-CH_2-CH=CH_2$

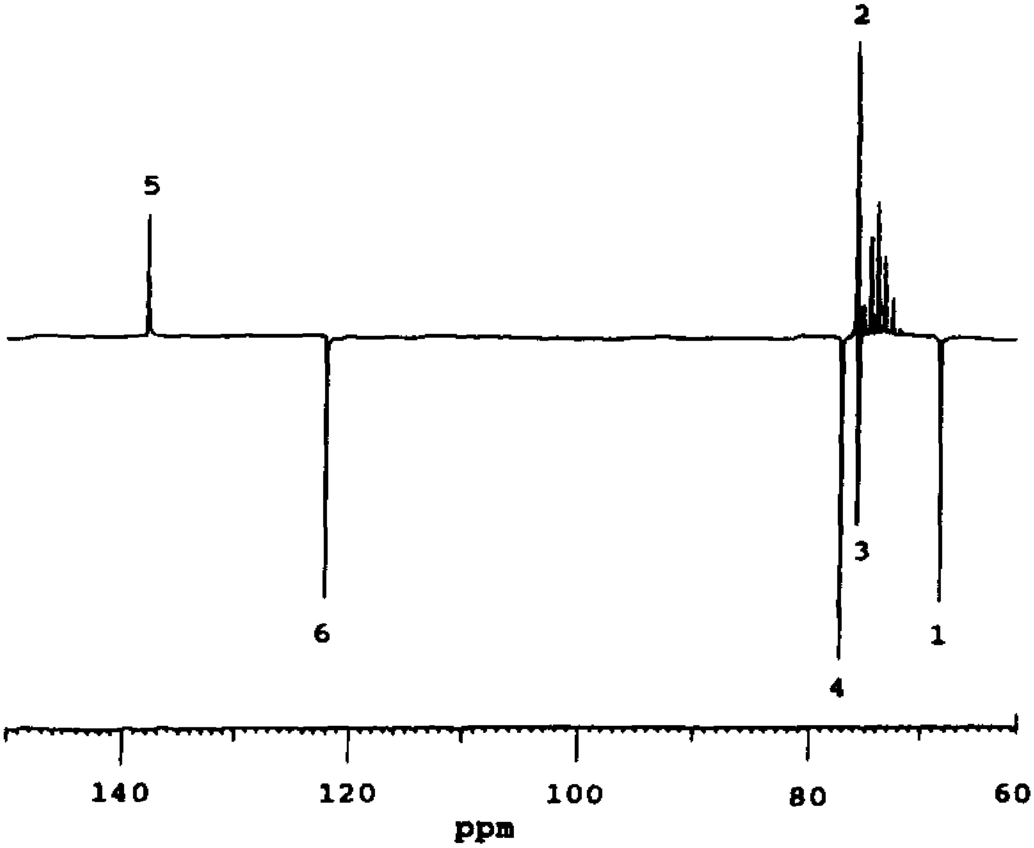


Fig. 4-14 ^{13}C DEPT spectrum of model compound in HFIP at 45°C

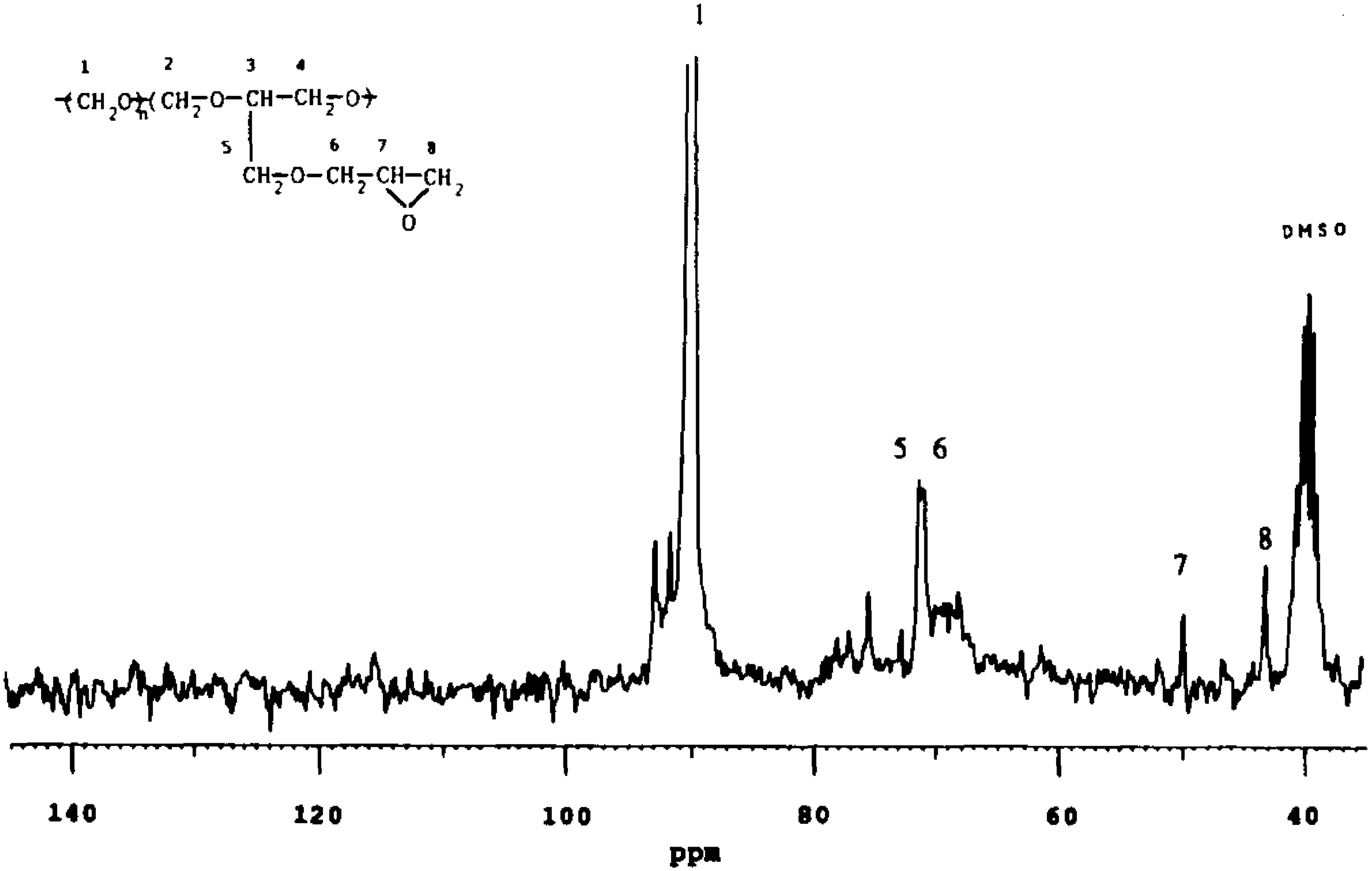


Fig. 4-15 ^{13}C spectrum of copolymer AGE-EP in DMSO-d_6 at 120°C.

diol peak at 63.6 ppm is not observed. It is not practical to observe ^{13}C NMR spectrum of copolymers in DMSO-d_6 at 120 °C due to severe degradation of copolymer at this temperature. Fig. 4-16 is a ^{13}C spectrum of copolymer in HFIP at 45 °C. The carbons of epoxy group at 47.2 and 54.3 ppm are clearly observed. No absorption at 67.2 ppm due to diol was found. For ^{13}C NMR spectra of all copolymers prepared, no diol peaks were found. The experimental results of epoxidation of copolymer TOX-AGE are also summarized in Table 4-3. More than 80% of pendant double bonds were converted to epoxy groups in most case.

In the process of epoxidation, acid catalyzed hydration of double bond is another possible reaction. A reaction of allyl glycidyl ether with 3-chlorobenzoic acid (mole ratio 1:1) in methylene chloride under the same reaction conditions as epoxidation was carried out to detect hydration. ^{1}H NMR spectrum of the reaction mixture shows that allyl glycidyl ether do not react at all, i.e. neither hydration reaction nor opening of epoxy group were observed. Thus, these reactions should not take place in the process of epoxidation of copolymers.

Methylene chloride used in this study is a common solvent employed in epoxidation[7] of organic compounds. In using this solvent, careful purge with nitrogen and evacuation to remove moisture are necessary to get reproducible results. Moisture may be absorbed on the crystal surfaces of copolymer and obstruct the reaction of

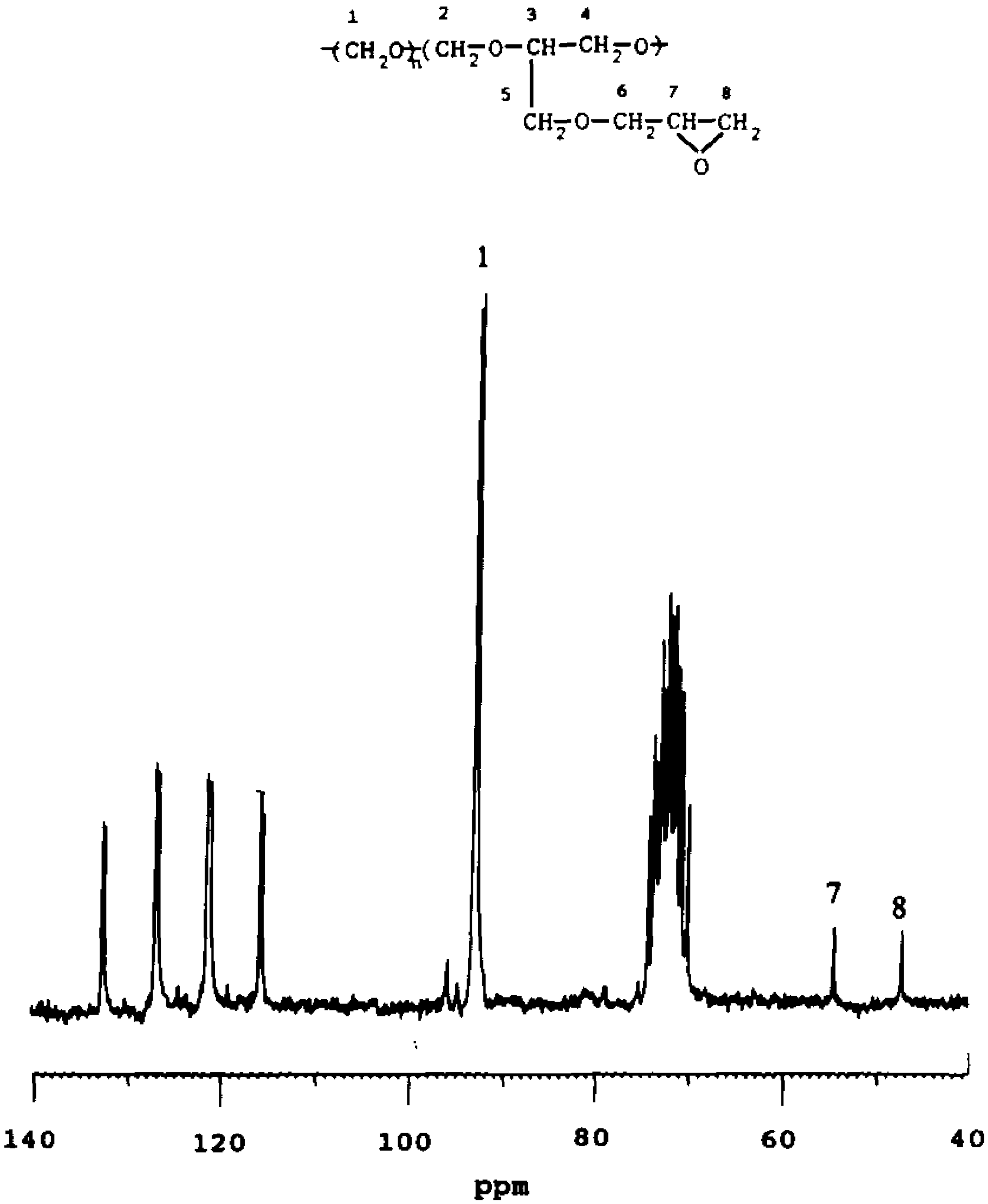


Fig. 4-16 ^{13}C spectrum of copolymer AGE-EP in HFIP at 45°C.

epoxidation. An exploratory reaction of epoxidation using a polar solvent, acetone, was carried out without nitrogen purging and evacuation. 31% of double bonds was converted to epoxy groups. Acetone can dissolve better both water and 3-chloroperoxybenzoic acid, thus acting as better solvent for epoxidation.

In the process of epoxidation, 3-chloroperoxybenzoic acid was used and converted to 3-chlorobenzoic acid, which must be removed completely from the copolymer. Trace amount of the acid causes severe degradation of the copolymer. Both the acid and peracid can be dissolved in acetone and removed.

4.3.5. Reaction of epoxidised copolymers

The epoxy copolymer react readily with a primary amine to form a copolymer with a secondary amine functionality:

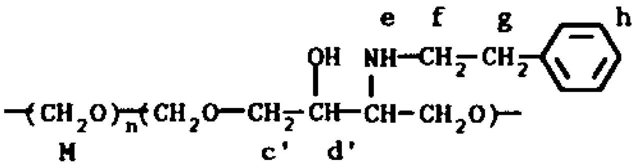


Fig. 4-17 shows a ^{1}H NMR spectrum of the product from copolymer with backbone epoxy groups reacting with phenethylamine in toluene at 95-100 °C for 6 hrs. The peak at 3.15 ppm due to the protons of the epoxy methine, **d**, as shown on Fig. 4-9 diminishes markedly, indicating that most of the epoxy group has reacted with phenethylamine. The

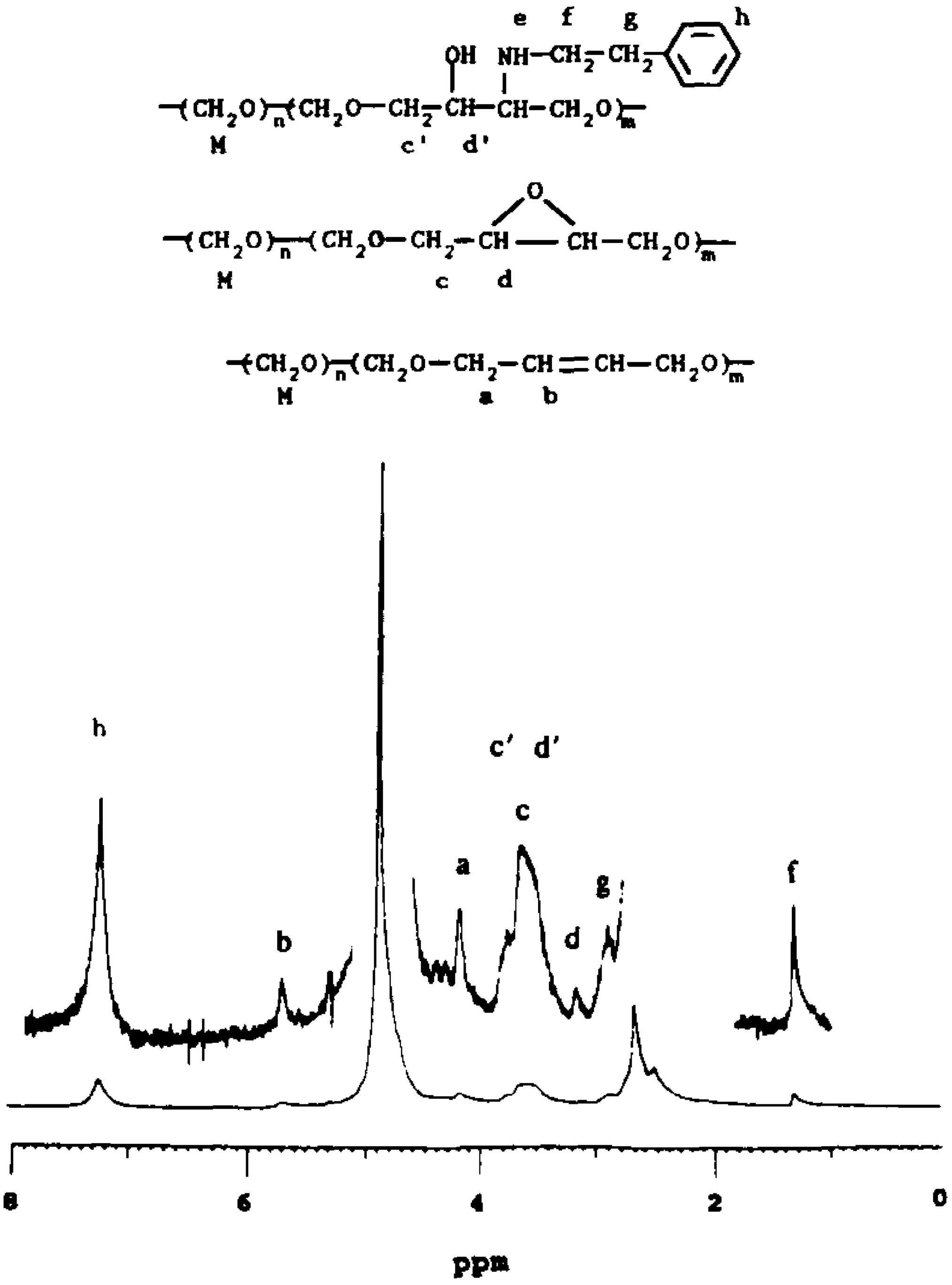


Fig. 4-17 ^{1}H NMR spectrum of copolymer DOP-EP reacted with phenethylamine in toluene at 95-100°C for 6 hrs.

intensive peak at 7.3 ppm is due to the phenyl groups (**h**). The conversion is estimated based the relationship:

$$\text{Conversion (\%)} = \frac{h/5}{h/5 + d} \times 100\%$$

This equation assumes that all the reacted epoxy functionality combined with amine. Based on its intensity, the incorporation of phenethylamine is estimated to be 64.8 % of the original epoxy group. For pendant epoxy groups, the reactivity is much higher. All of epoxy groups from epoxidized copolymer AGE reacted with phenethylamine in toluene at 95-100°C within 1 hour. However, the grafted copolymers show poor ^{1}H NMR resolution due to slight crosslinking.

Fig. 4-18 shows a ^{1}H NMR spectrum of copolymer AGE-EP having reacted with a secondary amine, N-benzylmethylamine. The peak **b** at 2.18 ppm due to methyl group of the amine is used to calculate the incorporation of amine (Table 4-4) using the equation:

$$\text{Conversion \%} = \frac{b/3}{b/3 + 1} \times 100\%$$

Peak **1** is located at 3.05 ppm (see also Fig. 4-11). The intensity of absorption **a** can also be used in a similar manner, giving conversion closed to that derived from **b**. The conversion of side chain epoxy group reacted with phenethylamine and backbone epoxy reacted with N-benzylmethylamine were estimated similarly. From the original and the unreacted epoxy absorption, the percentage of epoxy group reacted with amine can be calculated. It

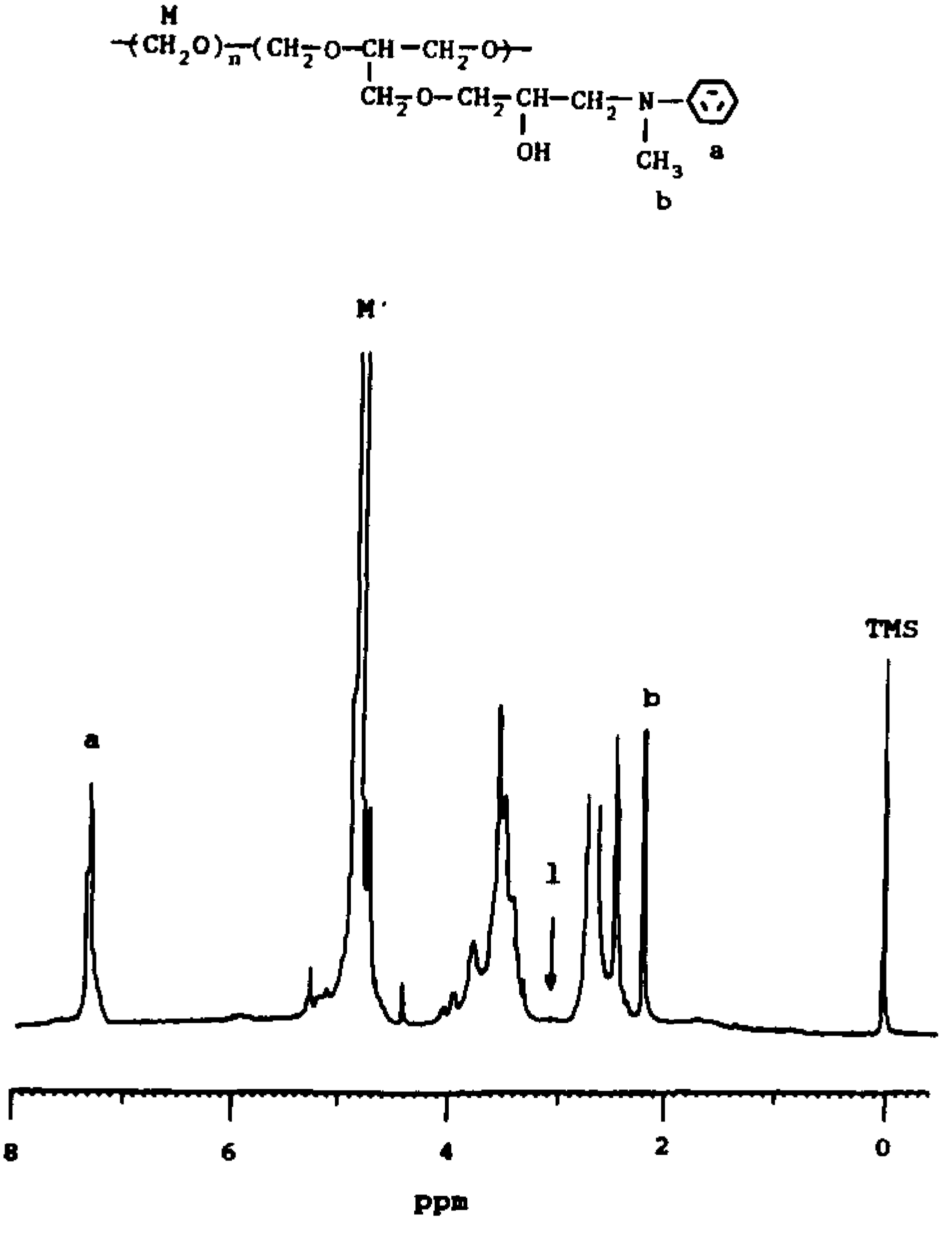


Fig. 4-18 ^{1}H NMR spectrum of copolymer AGE-EP reacted with N-benzylmethylamine in toluene at 95-100°C for 1 hrs.

appears that at least 90 % of the reacted epoxide gives the structure below:

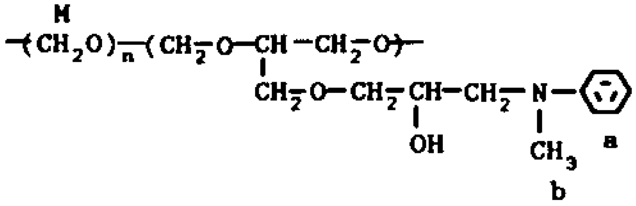
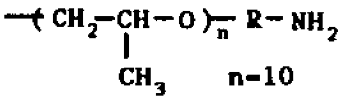


Table 4-4 summarizes the data of the reaction of epoxy groups with amines. For side chain epoxy copolymers, the primary amine, phenethylamine and the secondary amine, N-benzylmethylamine react completely with the epoxy group within 1 hour. However, in the case of the primary amine, the side chain epoxy copolymer leads to crosslink due to further reaction of the resulting secondary amine. For backbone epoxy copolymer, both amines react with epoxy group slowly. The secondary amine shows a reaction rate much slower than primary amine. For primary amine, 50 % of epoxy group reacted in 4 hrs, but 16 hrs is required for the same amount of the secondary amine to react. The data in Table 4-4 are plotted in Fig. 4-19.

A long chain amine, monoamine terminated polypropylene oxide (MW 600), was used to react with epoxy copolymers:



$$-(CH_2-\underset{CH_3}{CH}-O)_n-R-NH_2 \qquad n=10$$

Monoamine terminated polypropylene oxide

The absorption of methyl group of the propylene oxide units at 1.06 ppm was used to calculate the grafted propylene oxide side chain based on the n=10. For the reaction

Table 4-4 Reactivity of epoxy groups with phenethylamine and N-benzylmethylamine

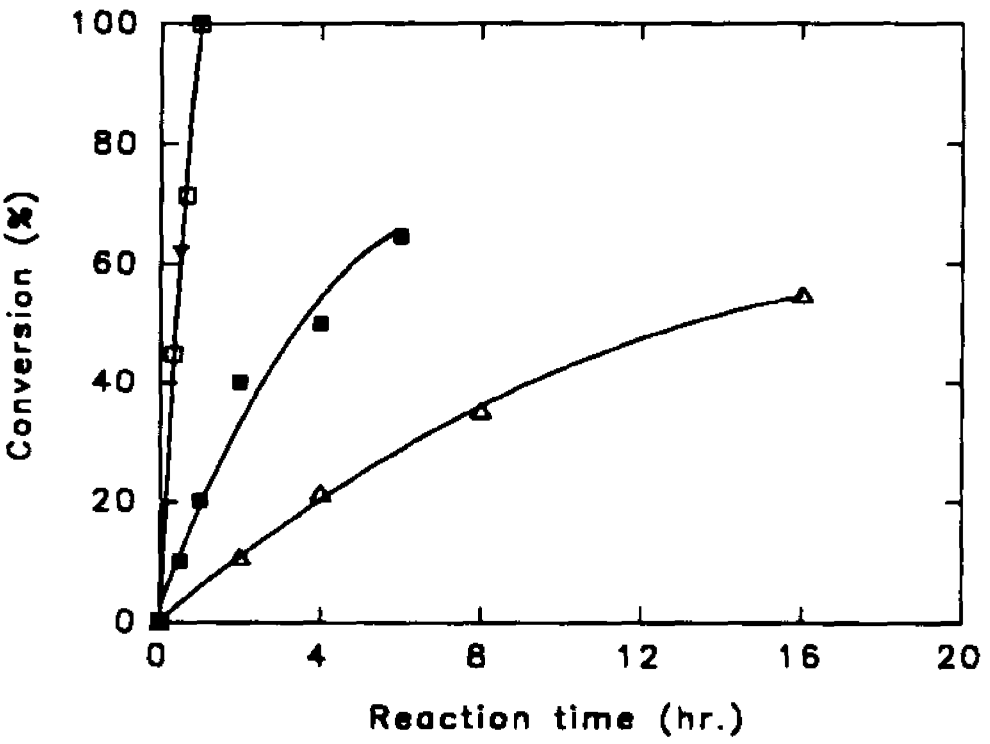
Epoxy Groups	Amine	reaction Time (hrs)	Conversion (%)
Side chain	Phenethylamine	0.5	62.0
		1	100.0
		2	100.0
Backbone	Phenethylamine	0.5	10.0
		1	20.1
		2	40.1
		4	50.0
		6	64.8
Side chain	N-benzylmethylamine	0.33	44.8
		0.66	71.5
		1	100.0
Backbone	N-benzylmethylamine	2	10.9
		4	21.5
		8	35.2
		16	54.9

Reaction condition: 95-100°C in toluene for 1 hr.

condition of 95-100°C and 20 hr reaction time in toluene, 53.6% of pendant epoxy group reacted, while only 11.2% of backbone epoxy group reacted. All the reactions above show that pendant epoxy group in copolymer is much reactive than backbone epoxy group in copolymer.

4.3.6. Thermal stability of epoxidized copolymers

Epoxy group is reactive toward acid and free radical, hence is expected to stabilize the copolymers. Fig. 4-20 shows the thermograms of copolymers with epoxy groups and amine groups. Curve 5 is copolymer of trioxane with dioxolane with incorporation of 1.4 mole % for comparison. Curve 1 for copolymer DOP-EP indicate better stability compared with copolymer DOP (see Fig. 4-8), even thought



▼ Side chain epoxy reacted with phenethylamine
□ Side chain epoxy reacted with N-benzylmethylamine
■ Backbone epoxy reacted with phenethylamine
△ Backbone epoxy reacted with N-benzylmethylamine

Fig. 4-19 Reactivity of Epoxy groups with primary and secondary amines.

the incorporation in the former is lower than that of the latter. Copolymer of AGE-EP (curve 4) is stable. The weight loss of copolymer AGE-EP (3.34 mole % incorporated) at 280 °C is about 3 %. For copolymer AGE (1.73 mole incorporation, see Fig. 2-6), the weight loss at this point is 7%. Curve 2 of copolymer DOP-EP reacted with amine almost overlap with curve 1 of copolymer DOP-EP. Copolymer AGE-EP with amine (curve 3) apparent to be more stable than copolymer AGE-EP. Epoxidation of copolymer requires the use of peracids. The by-product acid of this process must be removed thoroughly; trace amount of acid causes severe degradation of copolymer.

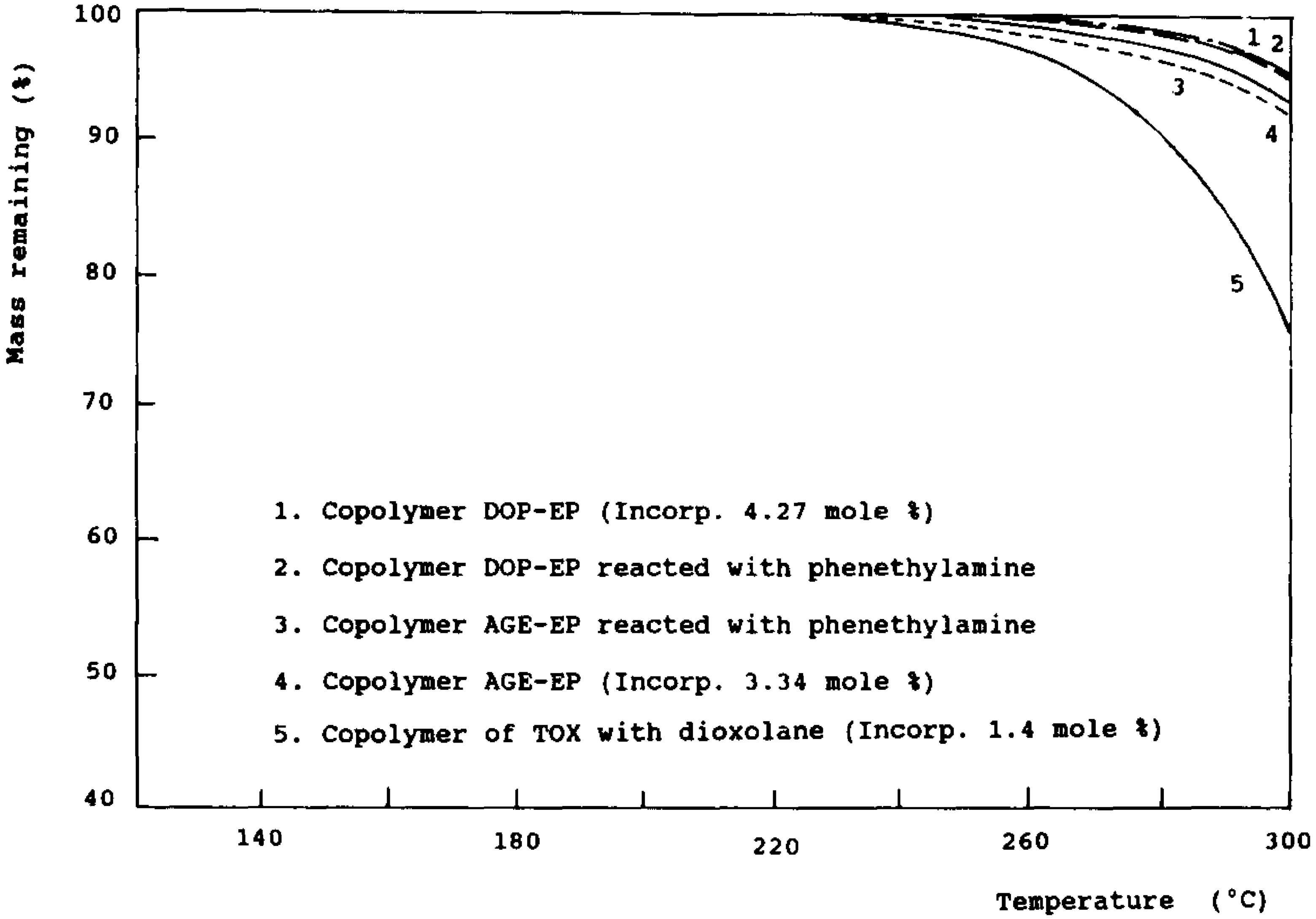


Fig. 4-20 TGA thermograms of copolymers

4.4. Conclusion

Cationic copolymerization of trioxane with allyl glycidyl ether (AGE) or 4-allyloxymethyl-1,3-dioxalane (AOMDO) gives thermally stable copolymers with pendant double bond. Copolymers with backbone or pendant double bond can be epoxidized to give copolymers with epoxy functional groups which are reactive for further modification. Hydrolysis of copolymer, e.g. copolymer of trioxane with 1,3-dioxep-5-ene, at 95~100 °C in sodium hydroxide heterogeneous aqueous suspension gives thermally stable copolymer. Both backbone and pendant epoxy groups are reactive toward amines, including primary and secondary amine. Pendant epoxy groups react much more efficiently.

The reactions of hydrolysis to remove the unstable end groups, epoxidation of double bonds and amination of epoxy groups of copolymer were carried out at 95-100°C in NaOH aqueous solution, 0-5°C in methylene chloride and 90-100°C in toluene respectively. The copolymer do not dissolve under these reaction conditions. Yet all reactions give good yield. This suggests that most of the comonomer units and the end groups of copolymer are located either on the surfaces of crystal or in the amorphous region.

5. Concluding Remarks

The goal of this investigation is to develop acetal copolymers with functional groups which are reactive for further modification. Three systems have been investigated.

Copolymers carrying pendant acrylate and hydroxyl groups were synthesized using 1,3-dioxane and glycerol formal derivatives as comonomers. Pendant acrylate and hydroxyl functional groups were demonstrated to be reactive for further modification. Both monomer units act as stable end groups and unzipping stoppers. However, glycerol formal system provide higher incorporation of functional groups and better survival of acrylate double bond. The addition of tertiary amine suppressed the opening of double bond and prevent the crosslink of copolymers in the process of copolymerization using $BF_3 \cdot Et_2O$ as initiator.

Polyacetals with backbone and pendant epoxy functional groups were synthesized through the epoxidation of acetal copolymer with backbone or pendant double bond. Acetal copolymers with pendant double bonds were synthesized using allyl glycidyl ether as comonomer. It was demonstrated that acetal copolymers with both pendant and backbone epoxy groups are reactive toward amines, including primary and secondary amines. The pendant epoxy groups have shown to be more reactive than the backbone epoxy groups. When primary amines react with epoxy copolymers, especially pendant epoxy copolymers, a slightly crosslinked copolymer was observed.

However, when secondary amine is used, no crosslink was observed. As expected, pendant epoxy groups were shown to be more reactive toward amine than acrylate. Among the three systems investigated, the epoxy copolymer system shows highest reactivity.

The study of crystallinity of copolymer and graft copolymer through DSC shows that comonomer units and graft chain lower the melting temperature and crystallinity of acetal copolymer. Graft, compared to comonomer incorporation, shows much more pronounced effect on both crystallinity and melting point.

Base on the observation of a number of reaction of the copolymer in suspension, one can conclude that most of the comonomer units in all three systems are located on the surface or amorphous part of polymer crystal. The significance of this observation is that the reactions for modification of acetal copolymers can be performed in heterogeneous system at lower temperature without disturbing the crystal structure. The possible degradation of acetal copolymer at high temperature can then be avoided.

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