Glycidyl Methacrylate–tert-Butyl Acrylate Copolymers: Synthesis, Characterization, and Thermal Studies

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Synopsis

Glycidyl methacrylate was copolymerized with tert-butyl acrylate in bulk at 60°C using benzoyl peroxide as free radical initiator. The copolymer composition was determined by chemical analysis as well as from ^{13}C-NMR data. The monomer reactivity ratios were calculated by using the YBR method. The number average sequence length of the copolymers was determined from ^{13}C-NMR data and compared with those obtained from reactivity ratios. The intrinsic viscosity of the copolymers was determined in DMF, and thermal stability as well as mechanism of thermal degradation of the copolymers were evaluated.

INTRODUCTION

Vinyl copolymers containing pendant epoxy groups provide a wide range of choice for chemical modification of parent polymers. The reactivity of the oxirane ring towards various nucleophiles is helpful for chemical modification of the basic polymer for various novel end uses. Copolymers based on glycidyl methacrylate (GMA) are thus of great value for binding enzymes and other biologically active species.[1,2] The sensitivity of the epoxy group to ionizing radiation renders these copolymers potential candidates for negative electron beam resists.[3]

As the various micro- and macro-physicochemical properties of these copolymers fundamentally influence their overall performance, in our program we intend to evaluate the properties of glycidyl methacrylate–alkyl acrylate copolymers. In our previous communications we reported the copolymerization behavior of GMA with various alkyl acrylates and characterization of the resulting polymers.[4-7]

In the present article we extended our studies on copolymerization of GMA with tert-butyl acrylate. In addition to evaluation of monomer reactivity ratios, the copolymers were characterized by various physicochemical techniques. The properties studied include microstructure of the copolymers by ^{13}C-NMR, intrinsic viscosity $[\eta]$, and glass transition temperature (T_g). The thermal behaviour of the copolymers was studied by thermogravimetry as well as by pyrolysis gas chromatography–mass spectrometry. The compositional effects on the overall properties of the copolymers were assessed.

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EXPERIMENTAL

Materials and Copolymerization

GMA and tert-butyl acrylate (tBA) were obtained from Fluka AG and were purified by distillation under reduced pressure over 4-Å molecular sieves. Benzoyl peroxide (BDH) was purified by recrystallization from methanol and a stock solution was made with chloroform. All the solvents used were reagent grade, obtained from BDH, and were purified by the standard procedure.[8]

Predetermined amounts of comonomers and initiator were mixed in reaction tubes and were freed of air by freeze–evacuation–thaw cycles from liquid nitrogen temperature. The copolymerization reactions were carried out at $60 \pm 0.1°C$. The details of polymerization and purification of the polymers have been described elsewhere.[4] To establish reproducibility, the reactions were carried out in duplicate with identical feed ratios. The compositions of the copolymers were determined by estimating epoxy group using hydrochloric acid–dioxane reagent[9] as well as from ^{13}C-NMR data.

Characterization of the Copolymers

The ^{13}C-NMR spectra of the polymers were recorded using a JEOL-JNM-FX 100 NMR spectrometer operating at 25.05 MHz in FT mode. In order to carry out a quantitative NMR study gated decoupling (NNOE) technique was employed. The details of operation conditions are given below:

Sample	—15–20% (w/v) solution in $CDCl_3$
Temperature of the probe	—50°C
Reference	—Center peak of $CDCl_3$ assigned as 77.0 ppm
Pulse width	—6 μs (≈30° flip angle)
Pulse delay	—5 s
Spectral width	—6250 Hz
16 K data points for Fourier transform.	

The above experimental conditions ensure the optimum parameters required for quantitative estimation of ^{13}C resonances.[10]

Intrinsic viscosities [η] of the copolymers were determined in dry DMF at $30 \pm 0.05°C$ using an Ubbelohde viscometer.

The glass transition temperatures (T_g) of the copolymers were determined using a thermomechanical analyzer (TMA) fabricated indigenously. The samples were cooled to liquid nitrogen temperature and the experiments were carried out by programmed heating at the heating rate of 8°C/min in nitrogen atmosphere.

Thermogravimetric analysis (TGA) of the copolymers was carried out using a DuPont 991 thermobalance in nitrogen atmosphere at a heating rate of 15°C/min.

Pyrolysis was carried out using a Philips curie point pyrolyzer. The head of the pyrolyzer was interfaced with the gas chromatograph to trap the degradable products automatically. The gas chromatograph used was a Varian Model 3700 with an injection needle insert adapted for a pyrolysis unit.

The column used was a chromosorb 102 porous polymer column (60/8 mesh, 6 ft $\times$ 1/8 in. O.D.). The temperature of the column was 200°C and the helium carrier gas flow rate was 2 mL/min. The pyrolyzed products were detected by flame ionization. The eluted pyrolysis peaks were identified by a Hewlett-Packard Model 5985A mass spectrometer coupled with a 5840A gas chromatograph by a jet separator for the packed column. The electron impact ionization source operated at an ionizing voltage of 70 eV and the ion source temperature was 200°C. A Hewlett-Packard Model 2648A data system was used to aid interpretation of mass spectra.

RESULTS AND DISCUSSION

Reactivity Ratios

The experimental conditions and results of the copolymerization are summarized in Table I. Using copolymer composition data the monomer reactivity ratios were calculated with the help of the YBR method,[11] which, because of its accuracy, is one of the superior methods among differential forms of copolymerization equations.[12]

The reactivity ratios for GMA (M_1) and tBA (M_2) in this copolymerization system were found to be

$$r_1 = 1.46 \pm 0.08 \quad \text{and} \quad r_2 = 0.28 \pm 0.04$$

Figure 1 shows the composition data as a function of monomer feed, which are in agreement with those calculated from reactivity ratio. The higher value of r_1 compared to r_2 indicates the preferential addition of GMA to the growing macroradical. From this it is evident that the copolymer chain consists of longer sequences of GMA units interrupted by tBA. Comparison of relative reactivity of other alkyl acrylates with GMA[4] indicates that the steric nature and polarities of the monomers are the governing factors for the reactivity of a given monomer.

TABLE I
Copolymerization of Glycidyl Methacrylate (M_1) with tert-Butyl Acrylate (M_2)[a]

Mole fraction (M_1) in the initial mixture	Percentage conversion	Mole fraction (m_1) in the copolymer	$[\eta]$ (dL/g)
0.279	6.3	0.461	1.90
0.279	6.5	0.456	
0.474	7.2	0.623	2.65
0.474	5.5	0.618	
0.677	6.4	0.825	3.30
0.677	5.9	0.822	
	$r_1 = 1.46 \pm 0.08,$	$r_2 = 0.28 \pm 0.04$	

[a] Polymerization conditions: catalyst, benzoyl peroxide (0.1% by weight of monomers); temperature, 60 $\pm$ 0.1°C.
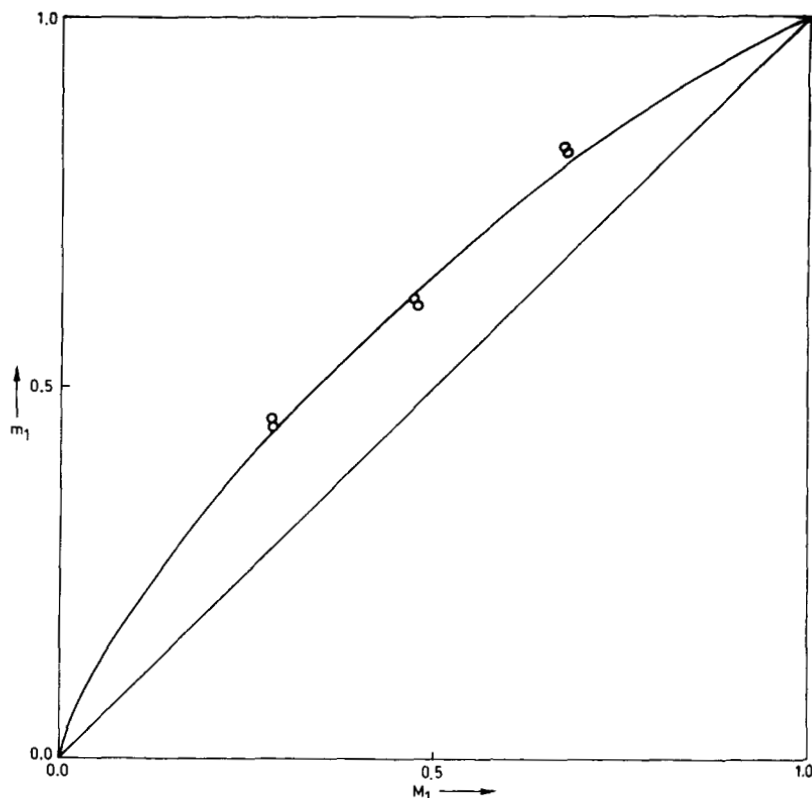
Fig. 1. Plot of mole fraction of GMA (m_1) using reactivity ratios.

^{13}C-NMR Study of Copolymers

High-resolution ^{13}C-NMR technique was employed to elucidate the microstructures of these copolymers. Various triad distributions were determined, which were used for estimating the sequence distribution of monomers in the copolymers.

The proton noise decoupled ^{13}C-spectra of poly(GMA), poly(tBA), and poly(GMA(A)-co-tBA(B)) are shown in Figures 2 to 4, respectively. The spectra of the homopolymers were interpreted with the aid of reported literature for analogous groups[13] while the interpretation of copolymer spectra were carried out by comparison of spectra of homopolymers. Inspection of the spectra of homopolymers reveals that while the stereochemical tacticity distribution is observed at carbonyl, quaternary α-carbon, and α-methyl carbon atoms of poly(GMA), it is only the backbone methylene carbon of poly(tBA) that gives tacticity information. In both cases the distribution is random.

The compositions of the copolymers were estimated from the peak intensities of $-OCH_2-$ carbon of GMA (65.9 ppm) and the ester methyl group of tBA (28.06 ppm), using the formula

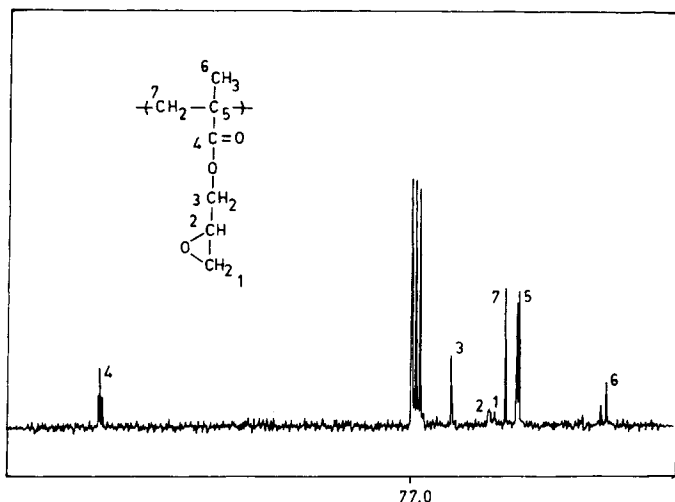$$\% \text{ GMA} = \left(\frac{S_1}{S_{2/3} + S_1}\right) \times 100 \tag{1}$$

Fig. 2.   ¹³C-NMR spectrum (25.05 MHz) of poly(glycidyl methacrylate).

where S_1 and S_2 are, respectively, the peak areas of carbon atoms of GMA and tBA under consideration. The intensity S_2 is divided by 3, since there are three equivalent methyl groups in the side substituent of tBA.

The α-methyl group of GMA, which resonates in the region of 17.16–18.72 ppm, was considered for determination of sequence distribution. Besides, the carbonyl carbon atoms of the two units resonate in different field strengths and the nature of the intensity pattern of the peaks is different for copolymers and homopolymers, indicating copolymeric effect. Various peaks were assigned to different GMA(A) centered triads. The copolymers show cotacticity phenomenon due to AAA block in the copolymer chain. The cotacticity phenomenon is further reflected in the backbone quaternary α-carbon resonance (due to GMA) in the 44.7- to 45.4-ppm range, which did not show any change in intensity pattern with variation in composition.
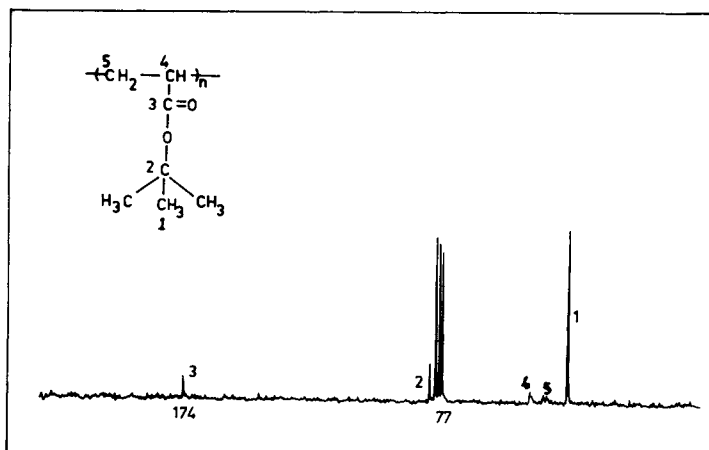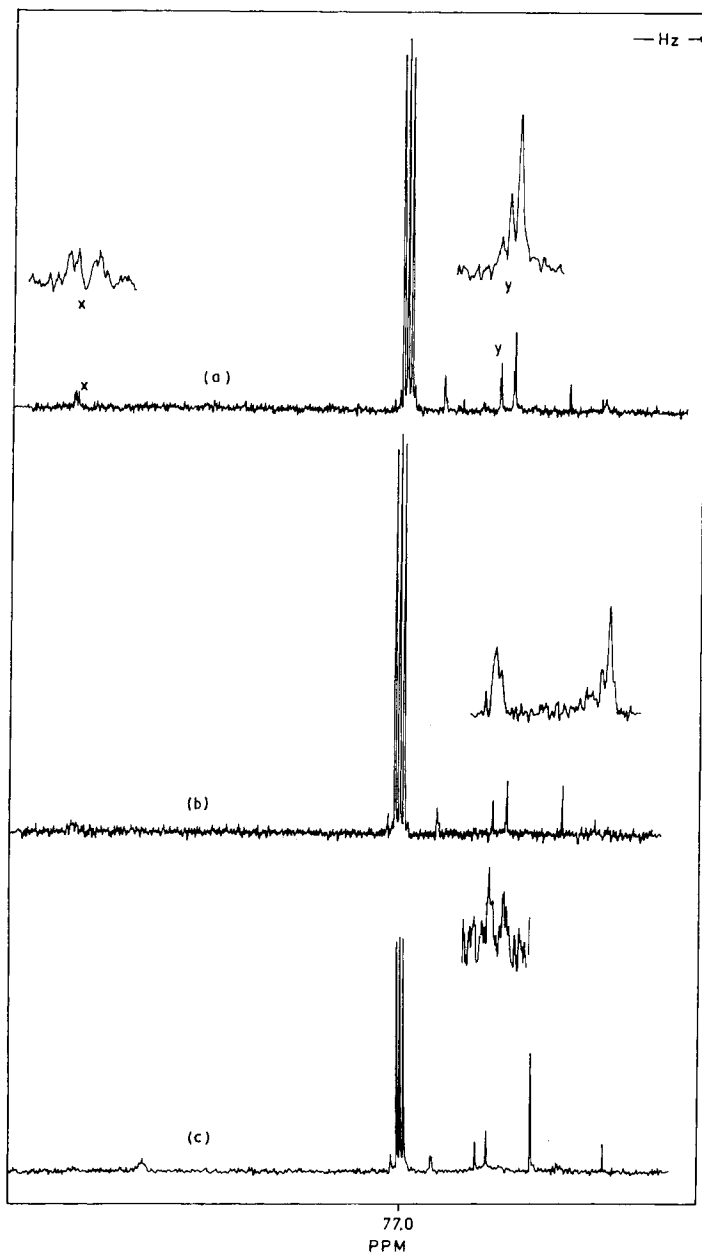

Fig. 3.   ¹³C-NMR spectrum of poly(tert-butyl acrylate).

GMA—tBA,(a) 82:18 ;(b) 62:38;(c) 46:54.

Fig. 4. ¹³C-NMR Spectra (25.05 MHz) of GMA–tBA copolymers.

Compositional triad sequence distribution was evaluated quantitatively by taking cotacticity into account.

At first, with the aid of reactivity ratio values, the number average sequence lengths ($\bar{N}_1$ and $\bar{N}_2$)were calculated using the pertinent equations[14,15]

$$\bar{N}_1 = \frac{1}{P_{12}} = r_1 \frac{[M_1]}{[M_2]} + 1 \qquad (2)$$

$$\bar{N}_2 = \frac{1}{P_{21}} = r_2 \frac{[M_2]}{[M_1]} + 1 \tag{3}$$

where $\bar{N}_1$ and $\bar{N}_2$ are the number average sequence lengths of the monomers 1 (GMA) and 2 (tBA), respectively. P_{12} and P_{21} are the conditional probabilities for cross propagation.

In addition, experimental determination of these sequence lengths was made possible by means of the various triad fraction values, using the equations[16]

$$\bar{N}_1 = (f_{212} + \frac{f_{112}}{2})^{-1} \tag{4}$$

$$\bar{N}_2 = (\frac{m_2}{m_1})\bar{N}_1 \tag{5}$$

where $f_{111} + f_{112} + f_{212} = 1$ for various GMA (1) centered triads and m_1 and m_2 are the mole fractions of the monomers GMA and tBA, respectively, in the resulting copolymer.

The number average sequence length values obtained by both methods are in fairly good agreement. All the results are summarized in Table II. The above experimental results suggest that the copolymerization process is random. Besides, GMA monomer is more reactive and forms larger blocks of GMA units in the chain. The GMA blocks in the copolymer exhibit tacticity phenomena having higher percentages of syndiotacticity. For the copolymers with higher tBA content, the resolution of the spectra was affected severely making difficult the quantitative estimation of various triad sequences.

Intrinsic Viscosity

The intrinsic viscosity $[\eta]$ of the copolymers determined in DMF is summarized in Table I. The data reveal that with increase in GMA content in the copolymer the $[\eta]$ value increases. This may be attributed to the fact that in the copolymerization system with higher GMA content the probability of termination of growing tBA radical by combination gets reduced with GMA as the penultimate unit, which imparts steric crowding on the reactive ends. As a result, with increasing GMA content the molecular weight of the copolymer increases. This is further evident by a higher r_1 value, which indicates a greater number of GMA units in the copolymer and hence high molecular weight.

Thermal Studies

Thermal behavior of these copolymers was assessed from their thermal degradation pattern using thermogravimetry, pyrolysis gas chromatography–mass spectrometry, and determination of glass transition temperatures.

TABLE II
Monomer Sequence Distribution of GMA(A)–tBA(B) Copolymers

Mole fraction of GMA in the feed	Mole fraction of GMA in the copolymer	A centered triad fraction			$\overline{N}_1$		$\overline{N}_2$	
		fAAA	fAAB	fBAB	Exp.	Calcd.	Exp.	Calcd.
0.677	0.822	0.629	0.275	0.102	4.29	3.92	1.31	1.55

Thermograms of the copolymers typically represent two-stage weight loss, the first stage being ascribed to elimination of isobutene and water resulting in anhydride formation (Figure 5). Further, with increasing GMA content in the copolymers the overall thermal stability of the polymers decreases. The decrease in thermal stability with increasing GMA content was ascribed to the fact that the epoxy groups are insensitive to thermally induced ring opening cross-linking. On the contrary, the presence of quaternary carbon atoms due to GMA moiety in the main chain facilitates decomposition by an unzipping mechanism. The reason behind the thermal stability of the polymers richer in tBA is twofold. First, the elimination of isobutene results in anhydride formation, which provides further thermal stability.[17] A detailed reaction scheme regarding the formation of anhydride followed by isobutene elimination is shown under GC–MS analysis of pyrolysis products. Moreover, the tertiary carbon atom of tBA provides sites for chain cross-
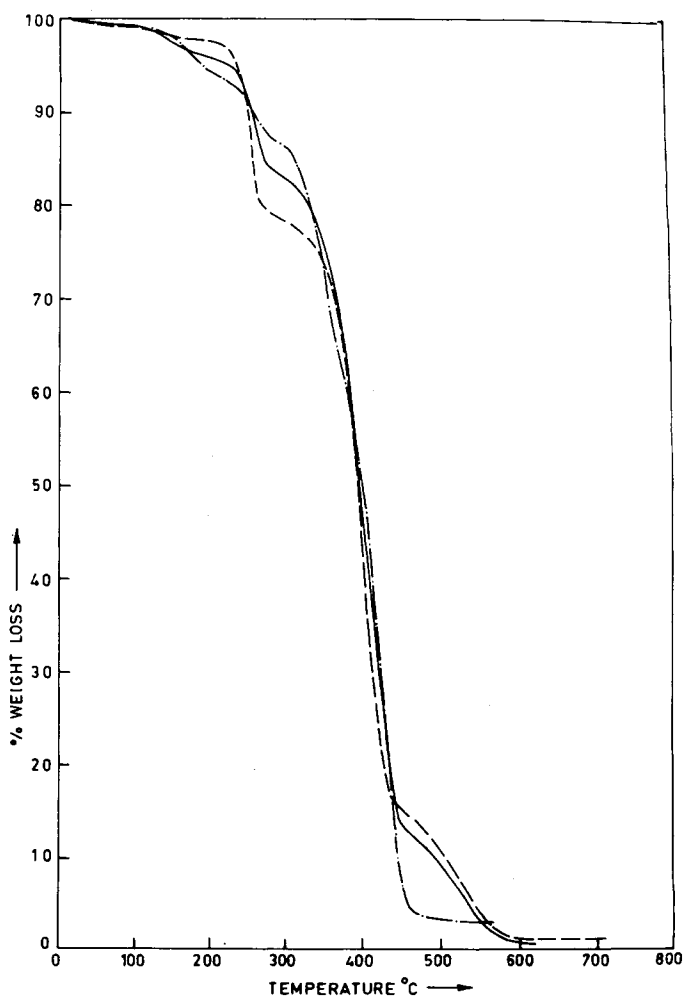
Fig. 5. Thermogravimetric analysis of GMA–tBA system. (- - -) GMA (0.822); (----) GMA (0.618); (—) GMA (0.461).

linking. The comparison of the effect of the nature of the alkyl side substituents on thermal stability indicates that with increase in branching of the alkyl side group the overall thermal stability decreases.[6] The data comprising the thermal properties of GMA–tBA copolymers are summarized in Table III.

Analysis of volatile products from pyrolytic decomposition of polymers provides useful information for understanding the mechanism of polymer degradation. The pyrogram of the degradation products obtained from GMA–tBA copolymers is shown in Figure 6. The various products obtained, as identified from mass spectral fragmentation pattern, are summarized in Table IV.

The formation of CO_2 and isobutene was ascribed to the fact that the initial step in the degradation of copolymers is likely to be scission at some unspecified point in the macromolecule. The reactive species generated in the first step would undergo subsequent reaction through a six-membered transition state involving the carbonyl group and hydrogen atom on the β-carbon atom of the ester group, yielding CO_2 and isobutene. The mechanism of this degradation process can be visualized as follows:
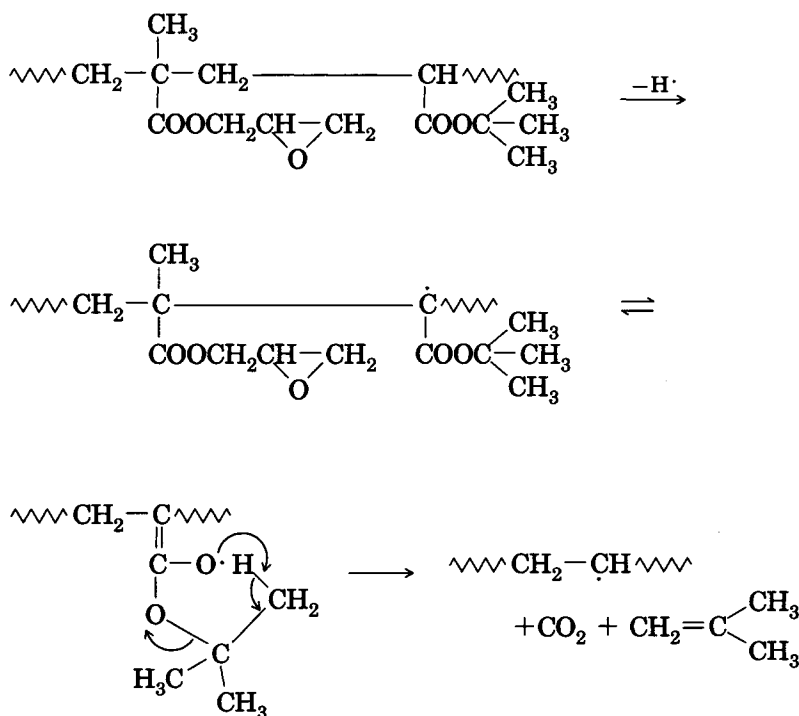
The formation of a large quantity of isobutene has also been ascribed to autocatalytic decomposition of the copolymer through a preformed acid. This would subsequently yield an anhydride by elimination of water. A similar type of mechanism for poly(tBA) degradation was put forth by Gras-

TABLE III
Thermal Behavior of GMA–tBA Copolymers

Mole fraction of GMA (m$_1$) in the copolymer	D^a_{max} (°C)	DT^b at 50% weight loss (°C)	IDPT^c (°C)	T_g (°C)
0.461	385	395	350	54
0.623	370	380	338	56
0.822	354	375	330	59

^{a} D_{max}: maximum decomposition temperature.
^{b} DT: decomposition temperature.
^{c} IPDT: integral procedural decomposition temperature.

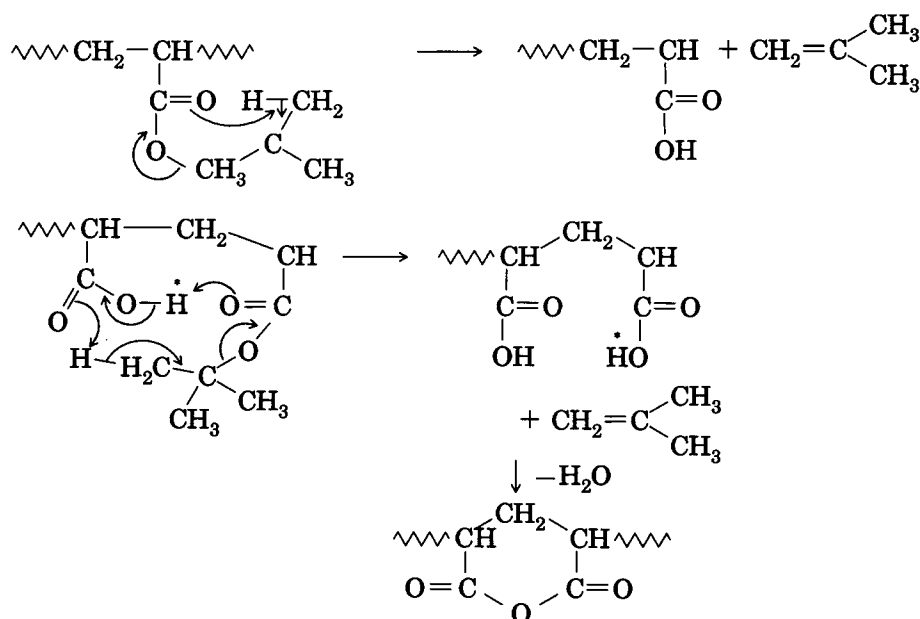sie et al.[17,18] The reaction scheme for this degradation process is shown below.
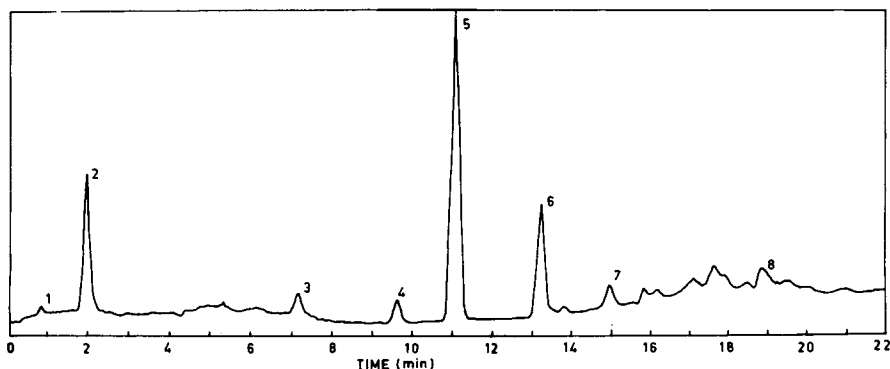
Fig. 6. Pyrogram of GMA–tBA (66:34) copolymer.

TABLE IV
Pyrolyzed Products of GMA–tBA (66:34) Copolymer Identified by GC–MS

| Product	Peak No.	Ion mass
CO	1	28
CO_2	2	44
$CH_3-CH=CH_2$	3	42
CH_3-CHO	4	44
$CH_2=C\overset{\diagup CH_3}{\diagdown CH_3}$	5	56
$CH_2=CH-CHO$	6	56
$CH_2=CH-CH_2OH$	7	58

Production of allyl alcohol, acrolein, and acetaldehyde has been explained on the basis of the degradation of the GMA part of the copolymer. The glycidyl radical produced from GMA undergoes the following scheme of reaction to produce the above-mentioned products.
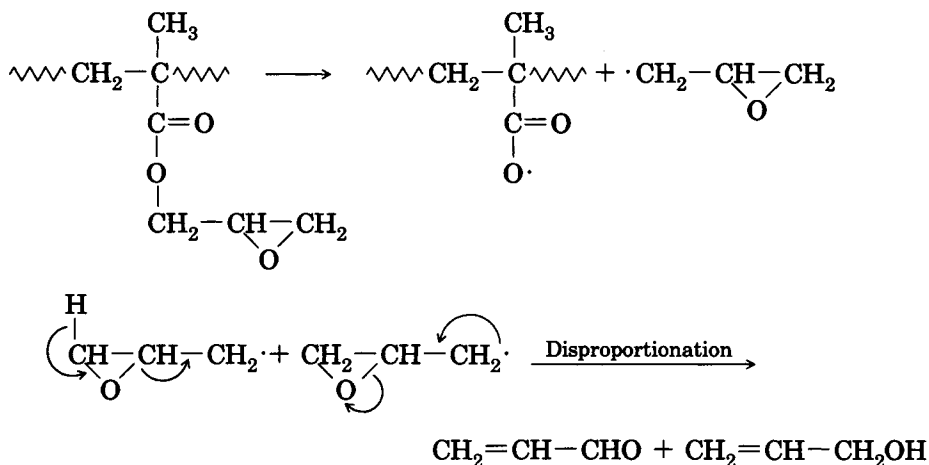
McBay and Tucker[19] predicted a similar type of mechanism for the reaction between alkoxy radicals to produce alcohol and aldehyde.

Similarly, the liberation of epoxide radical produces acetaldehyde with abstraction of hydrogen atom.
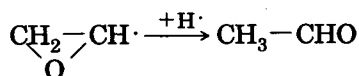
Glass transition temperatures (T_g) of these copolymers are shown in Table III. As expected, the T_g of the copolymers lie between the T_g of the corresponding homopolymers.

References

1. J. Kalal, *J. Polym. Sci. Polym. Symp.*, **62**, 251 (1978).

2. J. Korav, M. Navratilova, L. Shursky, J. Drobnik, and F. Svec, *Biotechnol. Bioengg.*, **24**(4), 837 (1982).

3. L. F. Thompson, L. Yau, and E. M. Doerrics, *J. Electrochem. Soc.*, **126**, 1703 1979).

4. P. K. Dhal, M. S. Ramakrishna, and G. N. Babu, *J. Polym. Sci. Polym. Chem. Ed.*, **19**, 1581 (1982).

5. P. K. Dhal, D. D. Deshpande, and G. N. Babu, *Polym. Prepr. Am. Chem. Soc. Div. Org. Coat. Plast.*, in press.

6. P. K. Dhal and G. N. Babu, *Polym. Prepr. Am. Chem. Soc. Div. Org. Coat. Plast.*, in press.

7. P. K. Dhal and G. N. Babu, *Angew Makromol. Chem.*, in press.

8. J. A. Riddick and U. Bunge, *Organic Solvents*, Wiley, New York, 1970.

9. G. M. Kline, *Analytical Chemistry of Polymers*, Part I, Interscience, New York, 1959.

10. F. W. Wehrli and T. Wirtilin, *Interpretation of Carbon-13 NMR Spectra*, Heydon and Sons, London, 1976, p. 264.

11. A. I. Yezrielev, B. O. Brokhima, and Y. S. Roskin, *Vysokomol. Soedin. Ser. A.*, **11**, 1670 (1969).

12. R. C. McFarlane, P. M. Reilly, and K. F. O'Driscoll, *J. Polym. Sci. Polym. Chem. Ed.*, **18**, 251 (1980).

13. L. F. Johnson and W. C. Jankowski, *Carbon-13 NMR Spectra*, Wiley–Interscience, New York, 1972.

14. P. W. Tidwell and G. A. Mortimer, *J. Polym. Sci. Polym. Chem. Ed.*, **3**, 369 (1965).

15. A. Rudin, K. F. O'Driscoll, and M. S. Rumack, *Polymer*, **22**, 740 (1981).

16. K. F. O'Driscoll, *J. Polym. Sci. Polym. Chem. Ed.*, **18**, 2747 (1980).

17. N. Grassie and J. R. MacCallum, *J. Polym. Sci. Polym. Chem. Ed.*, **2**, 983 (1964).

18. N. Grassie and D. H. Grant, *Polymer*, **1**, 445 (1960).

19. H. C. McBay and C. Tucker, *J. Org. Chem.*, **19**, 869, 1003 (1954).