

Synthesis of Copolymers of *tert*-Butyl Vinyl Ether with Maleic and Citraconic Anhydrides

Betül Kırıcı Denizli,^{1,3} Hatice Kaplan Can,¹ Zakir M.O. Rzaev,² Ali Güner¹

¹Department of Chemistry, Faculty of Science, Hacettepe University, Beytepe, 06532 Ankara, Turkey

²Department of Chemical Engineering, Faculty of Engineering, Hacettepe University, Beytepe, 06532 Ankara, Turkey

³Department of Technical Programmes, Gerede Vocational School, Abant İzzet Baysal University, Gerede, Bolu, Turkey

Received 20 April 2005; accepted 19 May 2005

DOI 10.1002/app.23577

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In the present study, the effects of charge-transfer complex formation and intramolecular fragmentation (side-chain lactonization) in radical copolymerization of *tert*-butyl vinyl ether (*t*-BVE) with anhydrides of maleic (MA) and citraconic (CA) acids and the structure–thermal behavior relationships of the resulting copolymers were examined using the ¹H-NMR, FTIR, DSC, and TGA analysis methods. It was shown that copolymerization under the chosen conditions proceeded through intramolecular frag-

mentation with the formation of γ -lactone units. Side-chain fragmentation of *t*-BVE–MA and *t*-BVE–CA copolymers also was confirmed by TGA and DSC analysis. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2455–2463, 2006

Key words: maleic anhydride; charge transfer complexes; radical polymerization; structure-property relations; copolymerization; FTIR; differential scanning calorimetry (DSC)

INTRODUCTION

Alternating copolymers of alkyl vinyl ethers with maleic anhydride (MA) have received significant attention because of their unique properties and wide range of applications such as adhesives, photocrosslinkable and photostetting resin compositions, photographic films, electrophotographic recording and glass fiber coatings, reversible shear thinning gels, detergents, viscosity improvers, flocculants, and cellular plastics (only *tert*-butyl derivative), as well as controlled-release coatings, medicinal tablet coatings, animal antidiarrhea capsules, and so forth.^{1–5} The complex-radical copolymerization of maleic anhydride with various functional comonomers is an effective method for the synthesis of functional macromolecules with given compositions, structures, and properties.¹ Reactive anhydride units in these copolymers can be used as a new site for the preparation of grafting and hyperbranched macromolecular architectures.² Some copolymers, specifically methyl vinyl and divinyl ether copolymers, show antitumor activity and the property of induced production of interferon in animals, which is potentially useful for inhib-

iting the growth of Friends leukemia virus.^{1–6} Anhydride-containing copolymers covalently linked to biomolecules have been used for the preparation of soluble enzyme complexes in solution⁷ and in diagnostics for the synthesis of soluble conjugates of nucleic acid probes.^{7–9}

Hallensleben¹⁰ found that *n*-butyl-, *iso*-butyl-, and *tert*-butyl vinyl ethers formed strong equimolar complexes with MA. Equilibrium constants vinyl ethers (K_c) depend on the isomeric form of the alkyl substituent in vinyl monomer and the temperature and nature of the solvent. For these 1:1 complexes, the values of K_c were determined under similar conditions (in CCl₄ at 20°C by UV method): $K_c = 0.56, 1.11, \text{ and } 2.12 \text{ L/mol}$ for the *n*-butyl, *iso*-butyl, and *t*-butyl derivatives, respectively. The maximum copolymerization rate also was observed at an equimolar monomer feed ratio. A series of *iso*-butyl vinyl ether–MA alternating copolymers were prepared in chloroform and methyl ethyl ketone for a wide range of monomer feed compositions with AIBN at 50°C by Fujimori et al.^{11,12} The equilibrium constant for the *iso*-BVE...MA complex determined by the UV method was found as 0.033 L/mol in chloroform and 0.023 L/mol in MEK. Both the results of the kinetic study on radical copolymerization and the ¹³C-NMR study on the microstructure of the copolymers, which predominantly showed configuration in the MA units, indicated participation of the complex in the copolymerization.^{11,12}

It was shown that *t*-alkyl permethacrylates and related monomers can serve as chain transfer agents through an addition–substitution mechanism.^{13,14} It

Correspondence to: H. Kaplan Can (kirci@hacettepe.edu.tr, hkaplancan@yahoo.com).

Contract grant sponsor: TÜBİTAK (Turkish National Scientific and Technical Research Council); contract grant number: MISAG-146.

was also reported that di-*tert*-butyl perfumarate (D-*tert*-BPF) can be radically homo- and copolymerized,^{15–17} but the elimination of the *tert*-butyl group during the polymerization of the D-*tert*-BPF–methyl methacrylate and D-*tert*-BPF–di-2-ethylhexyl itaconate systems made the polymerization mechanism more complicated.¹⁷

It is known that poly(*tert*-butyl vinyl ether-*alt*-MA) undergoes a unique acid-catalyzed rearrangement reaction, using $\text{BF}_3 \cdot (\text{OEt})_2$ or H_2SO_4 as a catalyst under the conditions of alcohol, benzene, or chloroform reflux. It was shown that the same rearrangement also occurred in the solid state at 180°C to produce both a poly(carboxylactone) and an isobutylene.⁵ Functional polymers containing *tert*-butoxy-carbonyl groups, such as homo- and copolymers of *N-tert*-butoxycarboxy maleimide and *p-tert*-butoxycarboxystyrene, also could undergo elimination (releasing isobutylene and carbon dioxide) in the presence of catalytic acids. This unique property enabled these polymers to be used as chemically amplified resists in lithography and in the generation of high-resolution image patterns.^{18,19} Some intramolecular reactions, including lactonization of the side-chain functional groups in acid solution, also have been observed in other anhydride-containing polymers such as copolymers of vinyl(allyl) acetates with MA.^{4,20,21}

Recently, results of the radical copolymerization of *tert*-butyl vinyl ether with anhydrides of maleic and citraconic acids were reported.²² In the present study, the effects of charge-transfer complex formation and intramolecular fragmentation (side-chain lactonization) on the radical copolymerization of *tert*-butyl vinyl ether (*t*-BVE) with anhydrides of maleic (MA) and citraconic (CA) acids were investigated, and a structure–thermal behavior relationship of the copolymers was examined using ¹H-NMR, FTIR, TGA, and DSC analysis methods.

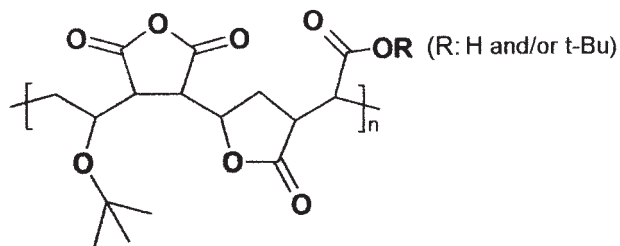
EXPERIMENTAL

Materials

t-BVE (Aldrich, Germany) was distilled under reduced pressure before use: bp 75.6°C, $n_D^{20} = 1.3979$, $d_4^{20} = 0.7618$. ¹H-NMR spectra: $\text{CH}_2=$, 1H quartet 6.51–6.46 ppm; $\text{CH}_2=$, two 2H quartets 4.16–4.12 and 3.91–3.89 ppm, respectively; and $(\text{CH}_3)_3\text{C}-$, 9H doublet 0.93 and 0.92 ppm.

MA (Fluka Chemie, Buchs, Switzerland) was purified by recrystallization from anhydrous benzene and sublimation in vacuum: mp 52.8°C. ¹H-NMR spectra: $\text{CH}_2=$, 2H singlet 7.34 ppm.

CA (Aldrich) was purified by distillation under vacuum before use: bp 213.5°C, $n_D^{20} = 1.4712$, $d_4^{20} = 1.2468$. ¹H-NMR spectra: $\text{CH}_2=$, 1H quartet 6.93–6.92 ppm; CH_3 , 3H doublet 2.19 and 2.18 ppm.



Scheme 1

α,α' -Azobisisobutyronitrile (AIBN; Fluka) was recrystallized twice from methanol: mp 102.5°C.

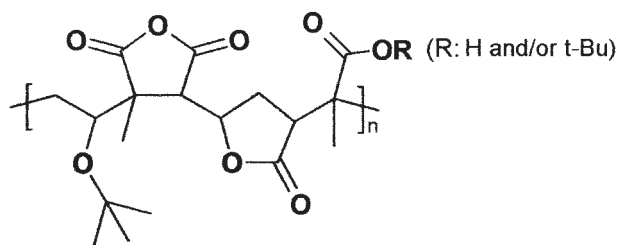
Copolymerization

Copolymerization of *t*-BVE with MA and CA was carried out in MEK in a nitrogen atmosphere with AIBN as a radical initiator at 65°C to conversions of 10%–12%. The copolymers produced were recovered by the addition of 10-fold excess methanol (for *t*-BVE–MA copolymer) or cold petroleum ether (for *t*-BVE–CA copolymer) and purified twice by reprecipitation from the MEK solution into methanol or cold petroleum ether and by washing with *n*-hexane and benzene. Purified copolymers were then dried in vacuum at 40°C to a constant weight. Copolymers were synthesized in the given reaction conditions ($[M]_{\text{total}} = 3.0$ mol/L, monomer molar ratio 50:50, $[\text{AIBN}] = 6.7 \times 10^{-3}$ mol/L, 65°C) and had the following average characteristics: *t*-BVE–MA fragmented copolymer $[\eta] 0.18$ dL/g in MEK at 25°C, $M_v = 21,000$, and $T_g = 184^\circ\text{C}$ with $\Delta H = 0.0021$ J/g (by DSC).

FTIR spectra (KBr pellet), cm^{-1} : 3610, 3200, and 2178 (OH stretching in COOH), 2980 (ν_{as} CH in CH_3), 2942 (ν_{as} CH in CH_2), 2920 (ν_s CH in CH_2), 2875 (ν_{as} CH in CH_3), 2860 (ν_s CH in CH_2), 1863 (ν_{as} C=O), and 1783 (ν_s C=O) for the anhydride unit; 1743 (C=O) for the γ -lactone or ester unit; 1634 (C=O) for the shifted conjugated C=O stretching band; 1470 (scissor vibrations of CH_2), 1430 (δ_{as} CH_3 antisymmetric deformation), 1395 and 1370 (δ_{as} CH_3 of *t*-butyl group), 1220–1180 (stretching of anhydride C–O–C), 1210–1200 (δCH_3), 1255–1240 (δCH_3 of *t*-butyl group), 1100 (broad stretching of C–O–C in lactone fragment), 920 (CH_3 rocking in *t*-butyl group), and 620–595 (δCH in CH–CH anhydride and lactone units).

¹H-NMR (400 MHz) spectra in CHCl_3-d_1 (δ , ppm): 0.43 (9H, CH_3 from *t*-butyl group), 1.34 (2H, CH_2 from *t*-BVE unit), 1.67 (2H, CH_2 from γ -lactone unit), 2.75 (1H, CH–CO from MA unit), 2.93 (1H, CH–CO from γ -lactone), 3.20 (1H, CH–O from *t*-BVE unit), 3.30 (1H weak singlet, CH–O from α -lactone unit).

t-BVE–CA fragmented copolymer $[\eta] 0.22$ dL/g in MEK at 25°C, $M_v = 30,200$, and $T_g = 176.5^\circ\text{C}$ with $\Delta H = 0.0054$ J/g (by DSC).



Scheme 2

FTIR spectra of this copolymer had bands similar to those of the *t*-BVE–MA fragmented copolymer.

¹H-NMR (400 MHz) spectra in CHCl₃-*d*₁ (δ, ppm): 0.88 (9H, CH₃ from *t*-butyl group), 1.45 (3H, CH₃ from CA unit), 1.80 (2H, CH₂ from *t*-BVE unit), 2.01 (2H, CH₂ from γ-lactone unit), 3.04 (1H, CH—CO from CA unit), 3.15 (1H, CH—CO from γ-lactone), 3.29 (1H, CH—O from *t*-BVE unit), 3.43 (1H weak doublet, CH—O from γ-lactone unit).

Measurements

FTIR spectra of the copolymers were obtained on a FTIR Nicolet 510 spectrometer (Nicolet Analytical Instruments, Madison, WI) in the 4000–400 cm⁻¹ range, with 30 scans taken at a resolution of 4 cm⁻¹. The ¹H-NMR spectra were recorded on a JEOL GX-400 (400 MHz) spectrometer with CH₃COCH₃-*d*₆, CHCl₃-*d*₁, or DMSO-*d*₆ as solvents at 35°C–50°C. Differential scanning calorimetric (DSC) and thermogravimetric (TGA) analyses of the copolymers were carried out with a DuPont V4.1C 2000 and a DuPont TA 951 Thermogravimetric Analyzer (Boston, MA), respectively, at a heating rate of 10°C/min under a nitrogen atmosphere.

Intrinsic viscosity [η] of the copolymers in THF and their molecular weight, *M_v*, were calculated by the following well-known equations^{23,24}:

$$[\eta] = \eta_{sp}/[c(1 + 0.333\eta_{sp})] \quad (1)$$

$$[\eta] = 7.56 \cdot 10^{-4} (M_v)^{0.55} \quad (2)$$

The relationship [eq. (2)] was obtained for the *iso*-BVE–MA copolymer in THF.⁴ The values of [η] in diluted solutions with copolymer concentrations of *c* < 1.0 g/dL were obtained using an Ubbelohde viscometer (Cannon–Ubbelohde, State College, PA) at 25°C ± 0.1°C.

RESULTS AND DISCUSSION

Charge transfer complex formation

The formation of charge transfer complexes (CTC) in donor (D)–acceptor (A) *t*-BVE–MA and *t*-BVE–CA monomer systems was confirmed by the results of ¹H-NMR (400 MHz) analysis of the spectra of the pure monomers and their mixtures ([D] ≫ [A]) at different ratios (Table I). Unlike the reported results for the *t*-BVE–MA system [7–10], equilibrium constants of 1:1 *t*-BVE...MA and *t*-BVE...CA CTCs (*K_c*) were determined in deuterated acetone, that is, under conditions similar to those used for copolymerization in MEK, using the well-known Hanna–Ashbaugh method²⁵:

$$1/[D] = \Delta_c K_c (\Delta_{obs})^{-1} - K_c \quad (3)$$

(for the conditions of [A] ≪ [D])

where [A] and [D] are acceptor and donor monomer concentrations, Δ_c is δ^f – δ^c (Δ_c is the difference between the free and complexed chemical shifts of acceptor protons in the complexing media), and Δ_{obs} is δ^f – δ^{obs} (Δ_{obs} is the difference between the free and observed chemical shifts of acceptor protons).

Thus, from a plot of 1/[D]_o (L/mol) versus (Δ_{obs})⁻¹ (1/ppm), shown in Table I, *K_c* values were determined to be 1.78 ± 0.1 and 0.58 ± 0.025 L/mol for the *t*-BVE...MA and *t*-BVE...CA complexes, respectively, at 35°C ± 0.1°C in CH₃COCH₃-*d*₆.

Observed relatively low value of *K_c* for the *t*-BVE...MA complex in acetone compared with that in CCl₄ (2.12 L/mol at 20°C)⁷ could be interpreted by the

TABLE I
¹H-NMR Data for Determination of Equilibrium Constants (*K_c*) of *t*-BVE...MA and *t*-BVE...CA Complexes in Deuterated Acetone at 35°C ± 0.1°C

Monomer feed			<i>t</i> -BVE–MA			<i>t</i> -BVE–CA		
[MA] or [CA] (mol/L)	[<i>t</i> -BVE] (mol/L)	[<i>t</i> -BVE] ⁻¹ (L mol)	δ _c ^{MA} ^a (ppm)	Δ _{exp} (ppm)	(Δ _{exp}) ⁻¹ (ppm) ⁻¹	δ _c ^{CA} ^a (ppm)	Δ _{exp} (ppm)	(Δ _{exp}) ⁻¹ (ppm) ⁻¹
0.1	1	1.00	7.314	0.025	40.0	6.922	0.006	166.7
0.1	2	0.50	7.309	0.030	33.3	6.919	0.009	111.1
0.1	3	0.33	7.307	0.032	31.0	6.917	0.011	88.0
0.1	4	0.25	7.304	0.035	28.8	6.916	0.012	82.0
0.1	5	0.20	7.303	0.036	28.5	6.915	0.013	78.0

^a δ_f^{MA} = 7.339 ppm and δ_f^{CA} = 6.928 ppm for the protons of free MA and CA, respectively.

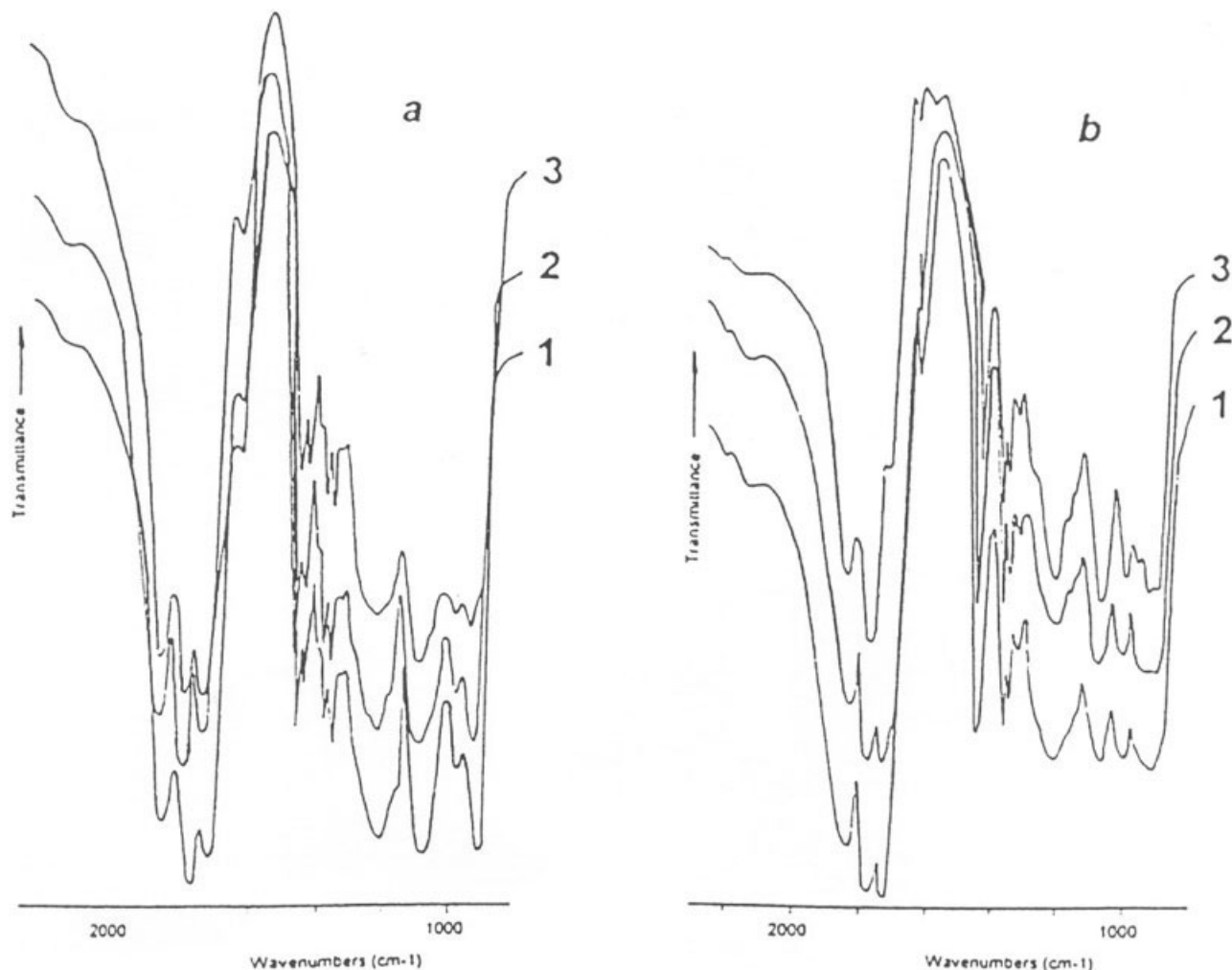


Figure 1 FTIR spectra (C=O region) of (a) *t*-BVE-MA and (b) *t*-BVE-CA synthesized in the various monomer ratios: [*t*-BVE] : [M_2] = 20 : 80 (1), 50 : 50 (2), and 80 : 20 (3).

solvent effect through the formation of a complex between the donor carbonyl group of the solvent and the acceptor double bond of MA ($K_c = 0.79$ L/mol at 25°C for MA...acetone and 0.62 L/mol at 60°C for MA...MEK complexes),²⁶ which essentially reduced the acceptor nature of MA and therefore reduced the equilibrium constant of the *t*-BVE...MA complex. The relatively low value of K_c for the *t*-BVE...CA complex also could be explained by a similar decrease in the electron-acceptor character of CA brought by a CH_3 group in the α position to the double bond.

Copolymerization via side-chain self-fragmentation

FTIR spectra of the fragmented copolymers [Fig. 1(a,b)] prepared using various monomer feed ratios contained new characteristic bands at 3610, 2178, and 1634 cm^{-1} (free $-\text{COOH}$) and 1735 cm^{-1} ($-\text{C}=\text{O}$ in a γ -lactone ring), which were absent in the spectrum of the *t*-BVE-MA alternating copolymer, prepared by copolymerization with AIBN in THF at 60°C.⁹

¹H-NMR spectra of these copolymers [Fig. 2(a,b)] also indicated that copolymerization under the chosen conditions proceeded through intramolecular fragmentation with the formation of a γ -lactone (1.67, 2.93, and 3.30 ppm for *t*-BVE-MA and 2.01, 3.15, and 3.43 ppm for *t*-BVE-CA fragmented copolymers). The observed self-fragmentation reaction was probably induced by the trace amount of free carboxyl groups from the anhydride monomer units and then by those forming after fragmentation.

Fragments of the ¹H-NMR spectra of the copolymers with different compositions are provided in Figure 3. As shown from this data, the intensity of the 1.45 (3H, CH_3 from CA unit), 1.62 (3H, CH_3 from fragmented unit), 1.80 (2H, CH_2 from *t*-BVE unit), and 2.01 (2H, CH_2 from γ -lactone) ppm peaks in the spectra of the *t*-BVE-CA fragmented copolymers visibly changed with the increase in *t*-BVE monomer concentration in the monomer feed, that is, the degree of fragmentation increased and was at the maximum at a

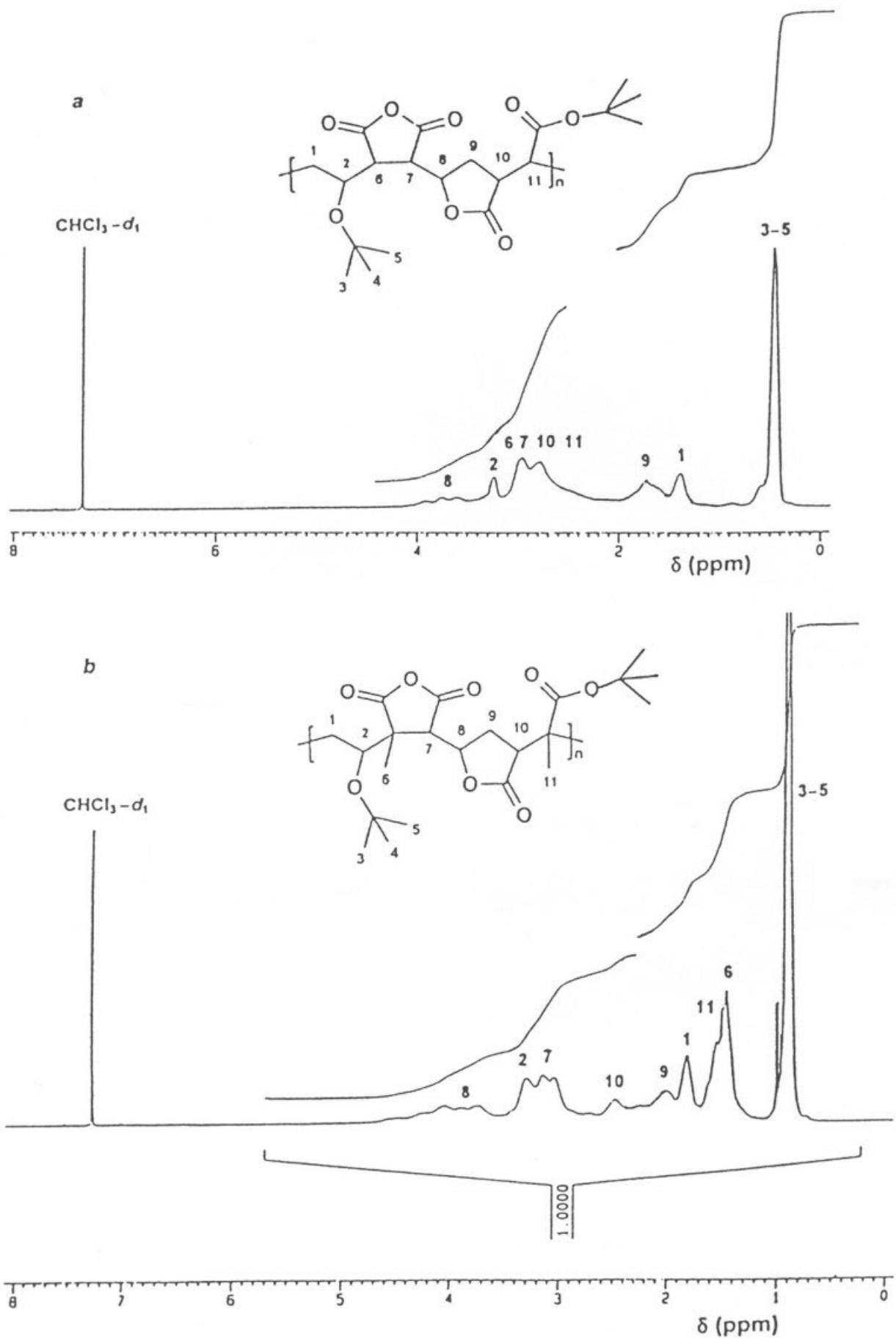


Figure 2 $^1\text{H-NMR}$ spectra of (a) $t\text{-BVE-MA}$ and (b) $t\text{-BVE-CA}$ copolymers in CHCl_3-d_1 at $50^\circ\text{C} \pm 1^\circ\text{C}$.

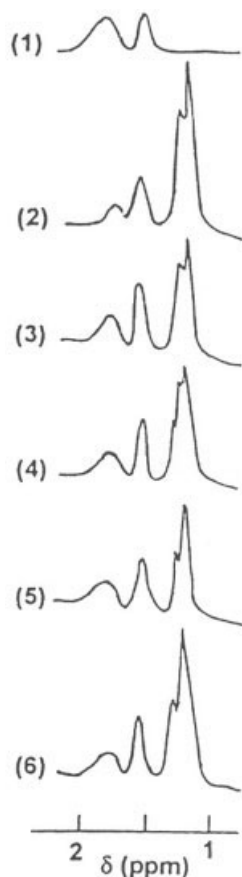


Figure 3 Fragments of $^1\text{H-NMR}$ spectra of (1) *t*-BVE-MA and (2–6) *t*-BVE-CA copolymers synthesized in the various monomer ratios: $[\textit{t}\text{-BVE}] : [\text{M}_2] = 0.25$ (2), 0.67 (3), 1.00 (4 and 5), 2.33 (5), and 4.00 (6).

50–60 mol % *t*-BVE concentration in the monomer feed (Fig. 4). Relatively high density of methylene groups (1.67 ppm 2H, CH_2 from γ -lactone) for the *t*-BVE-MA copolymer compared with that for the *t*-BVE-CA copolymer indicated a high degree of fragmentation in *t*-BVE-MA copolymer.

The compositions of the copolymers prepared using various monomer feed ratios were determined using the known NMR method²⁷ for the determination of styrene-MA copolymer compositions and were achieved by comparing the integrals of the *t*-butyl $[(\text{CH}_3)_3\text{C}]$, methyne (CH) or methyl (CH_3), and methylene (CH_2) group regions in the spectra of *t*-BVE, anhydride, and fragmented units, respectively. The mole fraction of the monomer unit in the copolymers (m_i) may be calculated by the following equations, where m_1 , m_2 , and m_3 are *t*-BVE, MA (or CA), and lactonized units, respectively.

$$\frac{Am_1(\text{CH}_3)}{A_{\text{total}}} = \frac{n_1m_1}{am_1 + bm_2 + cm_3} \quad (4)$$

$$\frac{Am_2(\text{CH or CH}_3)}{A_{\text{total}}} = \frac{n_2m_2}{am_1 + bm_2 + cm_3} \quad (5)$$

$$\frac{Am_3(\text{CH}_2)}{A_{\text{total}}} = \frac{n_3m_3}{am_1 + bm_2 + cm_3} \quad (6)$$

where Am_1 , Am_2 , and Am_3 are the normalized areas of per H from the *t*-butyl, methyne, and methylene groups of the respective monomer unit regions in $^1\text{H-NMR}$ spectra; A_{total} is the total area of protons in the copolymer; n is an integer of proton(s) in the functional group of the monomer or fragmented unit; a , b , and c are integers of protons in the monomer (m_1 and m_2) and fragmented (m_3) units, respectively; and m_1 , m_2 , and m_3 are the mole fractions of the monomer (m_1 and m_2) and fragmented units in the copolymer. For $(m_1 + m_2 + m_3) = 100$, monomer unit ratios can be calculated from eqs. (3)–(5) using the following simplified forms:

$$m_1/m_2 = n_2Am_1(\text{CH}_3)/n_1Am_2(\text{CH or CH}_3) \quad (7)$$

$$m_1/m_3 = n_3Am_1(\text{CH}_3)/n_1Am_3(\text{CH}_2) \quad (8)$$

$$m_2/m_3 = n_3Am_2(\text{CH or CH}_3)/n_2Am_3(\text{CH}_2) \quad (9)$$

An increase in the molar concentration of *t*-BVE in monomer feed m_3 increased the degree of fragmentation as a mole fraction of fragmented units (m_3) in the copolymers, which was calculated using $^1\text{H-NMR}$ data and eqs. (7)–(9) (Tables II and III). This showed the predominant role of the acid-catalyzed elimination reaction of *t*-butyl substituents in the form of isobutylene in the self-fragmentation reactions. As can be seen from a comparison of the m_3 values for both the *t*-BVE-MA and *t*-BVE-CA systems, the former system had a greater tendency toward self-fragmentation and alternation of monomer units. The appreciably low m_3

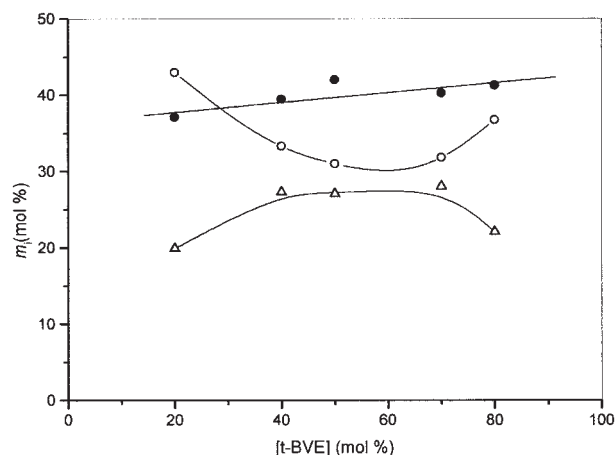
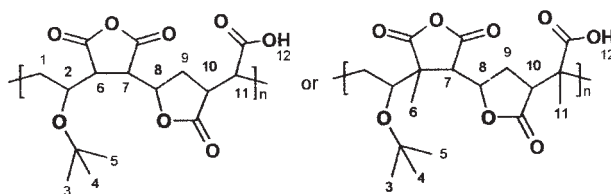


Figure 4 Monomer-fragmented copolymer composition plots for *t*-BVE-CA copolymers. $[\textit{t}\text{-BVE}]$ is the concentration of M_1 in the monomer feed, m_i is molar fraction of the m_1 (—●—) and m_2 (—○—) monomer units and the m_3 (—△—) fragmented unit in copolymer.

TABLE II
Integrals of Proton-Area Regions (from ¹H-NMR Data) for Functional Groups in *t*-BVE-*M*₂ (MA and CA) Copolymers Prepared in a Wide Range of Monomer Feed Ratios

Functional groups	Integrals of protons	Integrals of proton-area regions of copolymers (%)					
		<i>t</i> -BVE-MA 50:50	<i>t</i> -BVE-CA 20:80	<i>t</i> -BVE-CA 40:60	<i>t</i> -BVE-CA 50:50	<i>t</i> -BVE-CA 70:30	<i>t</i> -BVE-CA 80:20
CH ₃ in <i>t</i> -BVE unit	9	40.00	37.39	37.40	41.72	43.65	43.08
CH ₃ in anhydride unit	3	—	12.46	10.50	11.26	11.89	12.78
CH ₃ in fragmented unit	3	—	8.67	8.60	7.95	9.73	7.67
CH ₂ in <i>t</i> -BVE unit	2	8.89	8.31	8.31	9.27	9.70	9.56
CH ₂ in fragmented unit	2	11.94	5.77	5.73	5.30	6.49	5.11
CH—C—O (in <i>m</i> ₃ unit, 10) ^a	1	5.97	2.89	2.86	2.65	3.24	2.56
CH—C—O (in <i>m</i> ₃ unit, 11) ^a	1	5.97	—	—	—	—	—
CH—C—O (in <i>m</i> ₂ unit, 6, 7) ^a	2	10.86	—	—	—	—	—
CH—C—O (in <i>m</i> ₂ unit, 7) ^a	1	—	9.75	16.72	11.92	3.97	9.35
CH—O (in <i>m</i> ₁ unit, 2) ^a	1	4.43	4.15	4.16	4.63	4.85	4.79
CH—O (in <i>m</i> ₃ unit, 8) ^a	1	5.97	7.72	2.86	2.65	3.24	2.55
COOH (in <i>m</i> ₃ unit, 12) ^a	1	5.97	2.89	2.86	2.65	3.24	2.55

^a Numbers are positions of protons in copolymers.

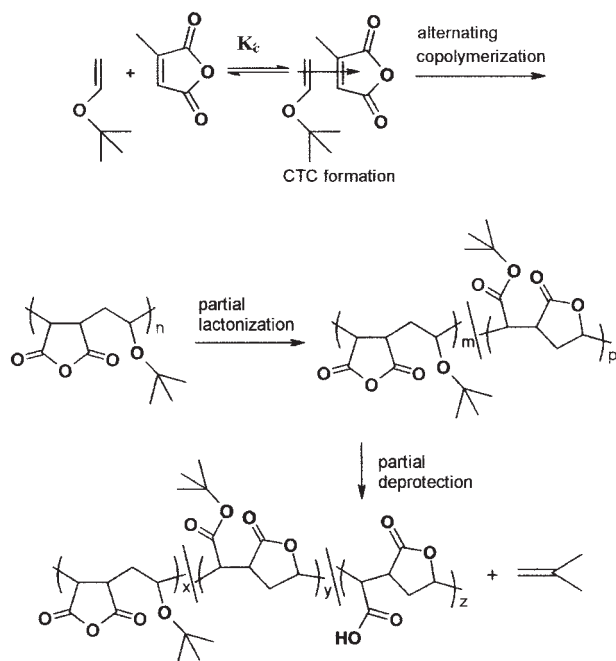


where *m*₁, *m*₂, and *m*₃ are *t*-BVE, MA (or CA), and lactonized units, respectively.

values obtained for *t*-BVE-CA can be explained by the relatively low electron-acceptor properties of the citraconic double bond and the relatively stable anhy-

dride ring in the reactions of macromolecular growth and fragmentation, respectively.

The general scheme of the CTC formation, alternating copolymerization, and self-fragmentation reactions follows:



Scheme 3

The copolymerization medium turned out to be an important factor in accomplishing these reactions. Thus, copolymerization of *t*-BVE with MA and CA in THF or chloroform as a relatively neutral solvent ($K_c = 0.086$ L/mol at 36°C for MA...THF bonds²⁸ and $K_c = 0.14$ L/mol at 60°C for MA...CHCl₃)²⁶) proceeded as clean alternating copolymerization, whereas alternating copolymerization of both monomer pairs under the same conditions but using MEK as the polar solvent was accompanied by partial intramolecular self-fragmentation. It is probable that the MEK solvent molecules formed CTCs with acceptor monomers ($K_c = 0.62$ L/mol at 60°C for MA...MEK through CH=CH and C=O bonds),²⁶ and the growing number of macroradicals increased the reactivity of anhydride ring in the fragmentation reaction.

Structure-thermal behavior relationships

Side-chain fragmentation (elimination of isobutylene) of the *t*-BVE-MA and *t*-BVE-CA copolymers also was confirmed by thermogravimetric analysis (TGA), results of which are illustrated in Figure 5.

TABLE III
Composition of *t*-BVE-MA and *t*-BVE-CA Copolymers Synthesized in a Wide Range of Monomer Feed Ratios in MEK Solvent at 65°C, [AIBN] = 6.7×10^{-3} mol/L, $[M]_{\text{total}} = 3.0$ mol/L in a Nitrogen Atmosphere

Monomer Feed (mol %) [<i>t</i> - BVE] [<i>M</i> ₂]		¹ H-NMR analysis (%)			Elemental analysis ^a (%)			Copolymer composition (mol %)		
		<i>Am</i> ₁ (CH ₃) ₃ C—	<i>Am</i> ₂ CH—CO or CH ₃	<i>Am</i> ₃ CH ₂	C	H	O	<i>m</i> ₁	<i>m</i> ₂	<i>m</i> ₃
30	70 (MA)				55.68	6.50	37.82			
50	50 (MA)	40.00	10.86	11.94	57.57	7.21	35.22	28.05	34.27	37.68
80	20 (MA)				57.77	6.95	35.28			
20	80 (CA)	37.39	12.46	5.77	59.26	7.44	33.30	37.12	42.98	19.90
40	60 (CA)	37.40	10.50	5.73	59.56	6.97	33.47	39.44	33.30	27.28
50	50 (CA)	41.72	11.26	5.30	60.08	6.26	33.66	41.98	30.98	27.04
70	30 (CA)	43.65	11.89	6.49	60.45	6.22	33.32	40.22	31.77	28.01
80	20 (CA)	45.40	13.47	5.39	61.11	7.24	31.65	41.25	36.72	22.03

^a Calculated values for the alternating (1:1) copolymer: C, 60.59%, and H, 7.12%, for the *t*-BVE-MA copolymer and C, 62.25%, and H, 7.60%, for the *t*-BVE-CA copolymer.

As evident from the TGA thermograms of these copolymers, they were stable up to 140°C, but above that temperature they underwent a visible loss of mass by partial elimination of *t*-butyl groups and then decomposition of *t*-BVE-MA and *t*-BVE-CA copolymers at about 287°C and 275°C, respectively. The *t*-BVE-MA and *t*-BVE-CA copolymers were estimated to have lost 4.5% and 6.6% of their mass, respectively, which was related to the loss in mass by the partial removal of isobutylene from the ester groups of the lactonized fragments.

The DSC thermograms revealed first endo effects at 139°C and 136°C, which was related to the partial deprotection of isobutylene from the side chains of *t*-BVE-MA and *t*-BVE-CA copolymers. The second endo effects, at 184°C, 176.5°C, and 176°C, were associated with the glass-transition temperatures of the corresponding copolymers.

CONCLUSIONS

We studied the charge-transfer complex formation and intramolecular fragmentation of *tert*-butyl vinyl

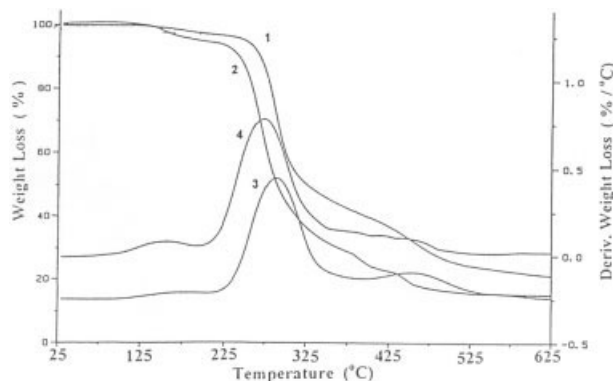


Figure 5 TGA (1 and 2) and DTG (3 and 4) thermograms of (1 and 3) of *t*-BVE-MA and (2 and 4) *t*-BVE-CA copolymers (heating rate 10°C/min under a nitrogen atmosphere).

ether (*t*-BVE) with anhydrides of maleic (MA) and citraconic (CA) acids by free-radical copolymerization. The equilibrium constants were found to be 1.78 ± 0.1 and 0.58 ± 0.025 L/mol for the *t*-BVE...MA and *t*-BVE...CA complexes, respectively, at $35^\circ\text{C} \pm 0.1^\circ\text{C}$ in $\text{CH}_3\text{COCH}_3-d_6$. The composition of the copolymers was determined by the NMR method. Copolymerization under the chosen conditions proceeded through intramolecular fragmentation with the formation of a γ -lactone. The thermostability of the *t*-BVE-CA copolymer was visibly lower than that of the *t*-BVE-MA copolymer, which was caused by the main-chain methyl group of the citraconic anhydride units. Generally, this reaction can be applied to a wide range of anhydride-containing polymers such as random or alternating copolymers, terpolymers, and cyclopolymers of MA and CA, which would enable the design of new macromolecular architectures with a given hyperbranched network structure and the synthesis of novel types of supercomposites with unique properties, which will be the subject of our future studies.

This study was carried out in accordance with the Polymer Science Program of the Departments of Chemical Engineering and Chemistry, Hacettepe University.

References

1. Rzaev, Z. M. O. *Prog Polym Sci* 2000, 25, 163.
2. Ulbrich, K., Etrych, T.; Chytil, P.; Jelinkova, M.; Rhova, B. *J Cont Release* 2003, 87, 33.
3. Kaplan Can, H.; Rzaev, Z. M. O.; Güner, A. *J Appl Polym Sci* 2003, 90, 4009.
4. Rzaev, Z. M. O. *Polymers and Copolymers of Maleic Anhydride*; Elm: Baku, 1984.
5. Cowie J. M. G. *Alternating Copolymers*; Plenum Press: New York, 1985; p 61.
6. Butler, G. B. *Cyclopolymerization and Cyclocopolymerization*; Marcel Dekker: New York, 1992.
7. Goldstein, L. *Anal Biochem* 1992, 50, 40.

8. Ladaviere, C.; Veron, L.; Delair, T.; Domard, A.; Pichot, D.; Mandrand, B. *J Appl Polym Sci* 1997, 65, 2567.
9. Ladaviere, C.; Veron, L.; Domard, A.; Pichot, D.; Mandrand, B. *J Appl Polym Sci* 1999, 71, 927.
10. Hallensleben, M.L. *Makromol Chem* 1970, 144, 267.
11. Fujimori, K.; Organ, P. P.; Costigan, M. J.; Craven, I. E. *J Macromol Sci Chem* 1986, A23, 647.
12. Hao, X.; Fujimori, K.; Tucker, D. J.; Henry, P. C. *Eur Polym J* 2000, 36, 1145.
13. Chaumont, P.; Colombani, D. *Macromol Chem Phys* 1995, 196, 947.
14. Colombani, D.; Chaumont, P. *Polymer* 1995, 36, 129.
15. Colombani, D.; Zink, M. O.; Chaumont, P. *Macromolecules* 1996, 29, 819.
16. Sato, T.; Matsumoto, Y.; Tanaka, H.; Ota, T. *Makromol Chem* 1987, 188, 769.
17. Sato, T.; Sato, M.; Seno, M. *J Appl Polym Sci* 2000, 75, 218.
18. Thompson, L. F.; Willson, C. G.; Tagawa, S. J., Eds. *Polymers for Microelectronics*; ACS Symposium Series 537; American Chemical Society: Washington, DC, 1994.
19. Ahn, K. D. F. In *Polymer Materials Encyclopedia*; CRC Press: Boca Raton, FL, 1996; Vol. 4, p 2621.
20. Kameda, J.; Hayoti, K. *J Chem Soc Japan Ind Chem Sec* 1968, 71, 557, 36A.
21. Chitanu, G. C.; Skouri, M.; Schosseler, F.; Munch, J. P.; Carpov, A.; Candaua, S. J. *Polymer* 2000, 41, 3683.
22. Rzaev, Z. M. O.; Kaplan Can, H.; Kirci, B.; Güner, A. *Abstr. Europolymer Congress (EPF) Radical Copolymerization of *t*-Butyl Vinyl Ether with Maleic and Citraconic Anhydrides*; Eindhoven, The Netherlands, July 15–20, 2001.
23. Solomon, O.; Gottesman, F. B. *Makromol Chem* 1967, 104, 177.
24. Endo, R.; Iimura, H.; Takade, M.; Kagaku K. *Chem Abstr* 1971, 29(1), 44; 1972, 76,141390h.
25. Hanna, M. W.; Ashbaugh A. L. *J Phys Chem* 1964, 68, 811.
26. Dodgson, K.; Ebdon, J. R. *Eur Polym J* 1977, 13, 791.
27. Cameron, N. R.; Cowie, J. M. G.; Ferguson, R.; McEwan, I. *Polymer* 2000, 41, 7255.
28. Ida, T.; Takahashi, S.; Utsumi, I.; Zasshi, Y. *Chem Abstr* 1969, 89, 517.