Characterization of Alternating Copolymers of Vinyl Ethers

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CHARACTERIZATION OF ALTERNATING COPOLYMERS OF VINYL ETHERS

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ABSTRACT

Copolymerization of methyl 2-cyano-3-phenyl-2-propenoate (MCP) and 2-phenyl-1,1-dicyanoethene (PDE) with ethyl, n-butyl, i-butyl, 2-chloroethyl, and phenyl vinyl ethers in broad ranges of comonomer ratios always produces copolymers of an equimolar composition. The alternating structure of these copolymers was established by elemental analysis and by infrared, ^{1}H- and ^{13}C-NMR spectroscopy. Microstructure analysis of the copolymer of PDE and phenyl vinyl ether, as deduced from ^{1}H and NOESY ^{13}C-NMR data, demonstrated the formation of alternating monomer structures with different orientations of the monomer units. Additional characterization of the copolymers was carried out by DSC and TGA. The order of decreasing T_g values, ethyl > phenyl > 2-chloroethyl > i-butyl > n-butyl vinyl ether, is the same for both MCP and PDE.

INTRODUCTION

Copolymerization of monomers with donor and acceptor properties results in the formation of products with predominantly alternating monomer structures [1]. A significant research effort has been devoted to the investigation of the controversial propagation mechanism of these polymerization reactions [2–4]. These copolymers can exhibit interesting physical properties that can contribute to their alternating structure. For example, poly(vinyl acetate-*alt*-vinylidene cyanide) copolymer exhibits significant piezoelectricity at room temperature which is attributed to the ability of the dicyano dipole to be oriented under an applied electric field [5]. Hall and his coworkers [6] reported that alternating copolymers of trisubstituted alkenes carrying cyano and carbomethoxy groups can undergo chain scission reactions owing to the electron-withdrawing groups and severe steric hindrance. Such polymers have improved reactive-ion etch resistance which could prove useful for the manufacture of microelectronics test structures and devices.

In the past we prepared new alternating copolymer structures with a high content of cyano and carbomethoxy groups via radical copolymerization of 2-cyano-3-phenyl-2-propenoate (MCP) and 2-phenyl-1,1-dicyanoethene (PDE) with electron-rich monosubstituted alkenes. We attempted to correlate the microstructure and properties of the copolymers with the chain propagation mechanism [7, 8]. In the preceding article [9] the results of an investigation regarding the solution radical copolymerization of MCP and PDE with ethyl (EVE), *n*-butyl (nBVE), *i*-butyl (iBVE), 2-chloroethyl (CEVE), and phenyl (PVE) vinyl ethers were reported. We found that the copolymers have an equimolar composition in broad ranges of monomer ratios.

The present work describes the characterization of these copolymers which most likely have a predominantly alternating structure.

EXPERIMENTAL

The copolymer samples were prepared in ethyl acetate at 70°C using 0.0045 mol/L AIBN as initiator at 2 mol/L total monomer concentration [9]. Crude copolymers, precipitated in methanol, were filtered by suction using sintered glass crucibles. The copolymers were washed repeatedly and dried in a vacuum oven at 70°C for 100 hours. An attempt to polymerize nBVE under the same conditions gave no solid polymer. Evaporation of the mixture gave an oil-like residue which was washed with ethanol and dried under reduced pressure.

Elemental microanalysis (C, H, N) of the copolymer samples was performed by Schwarzkopf Microanalytical Laboratory, Inc., Woodside, New York, and copolymers compositions were estimated based on the analysis.

IR spectra of the copolymers (as KBr pellets) were recorded with an IBM model FT-IR-32 spectrometer (resolution: 4 cm^{-1}). NMR spectra of 4–10% polymer solutions in chloroform-*d* were recorded at ambient temperature with a Bruker AC-200 spectrometer operating at 200.13 MHz for ^{1}H and 50.33 MHz for ^{13}C. Chemical shifts are reported referenced to chloroform-*d*. Proton spectra utilized 16K data points with a sweep width of 3600 Hz adjusted so that no quaditive images affected the spectra. A sweep width of 13.5 kHz and 32K data points were used for

the ^{13}C-NMR spectra. The 90 pulse widths were 7.5 μs for proton using a 5-mm dual ^{1}H-^{13}C probehead and 20.5 μs for carbon with a 15-mm dual ^{1}H-^{13}C probehead. Relaxation delays were at least 5 times the longest T^1 value in each spectrum. The DEPT spectra were obtained with an evolution delay of 3.704 ms to produce negative methylene and positive methine and methyl ^{13}C resonance signals with no quaternary carbon resonance. The JMODXH spectra (variable delay of 3.704 ms) were obtained to identify quaternary carbons. Proton-carbon correlation spectra were run using the standard XHCOR Bruker program. The carbon domain used 1K data points covering 10 to 100 ppm, and the proton domain used 1/4K data points covering 0 to 8 ppm. Delays were adjusted for maximum polarization and observation of all multiplicities ($D_3 = D_4 = 3.704$).

DSC analysis was performed using a DuPont 9900 Thermal Analyzer with 910 DSC module and a Polymer Laboratories Thermal Analyzer STA 625. A sample of 10-15 mg, crimped in an aluminum pan, was heated at 10°C/min in nitrogen. Glass transition temperatures (T_g) were determined from the thermogram on the third recycle run.

Thermogravimetric analysis (TGA) was performed with a DuPont 951 TG Analyzer at a heating rate of 10°C/min in static air (sample size: 5-15 mg).

RESULTS AND DISCUSSION

The MCP and PDE equimolar copolymers with the vinyl ethers are white, fine powders, soluble in methyl ethyl ketone, ethyl acetate, acetone, benzene, toluene, chloroform, and dimethylformamide; they are insoluble in hexane and cyclohexane. Since no homopolymers were detected after homopolymerization of the monomers in the presence of AIBN, no extractions by selected solvents on the copolymers were performed.

The copolymers' structure was analyzed by IR and NMR spectroscopy.

IR Spectra

Figure 1 shows infrared spectra of MCP and PDE copolymers with n-butyl vinyl ether. The spectra of both copolymers have a distinct band in the 2245-2250 cm^{-1} range which is common for polymers containing nitrile groups in side chains. The carbonyl group of MCP absorbs in the 1746-1748 cm^{-1} range. The 1450-1650 cm^{-1} region shows several overlapping bands of CH$_2$, CH$_3$ groups, and aromatic rings. A strong 1235-1245 cm^{-1} band corresponds to the C—O stretching mode in the MCP methoxy group. The band due to the ether group appears in the 900-1200 cm^{-1} region. All spectra of the copolymers show a band in the 700-750 cm^{-1} range, characteristic of the aromatic C—H out-of-plane mode (MCP and PDE).

^{1}H-NMR Spectra

Typical 200-MHz ^{1}H-NMR spectra of the copolymers are represented by the spectra of MCP-nBVE and PDE-nBVE copolymers (Fig. 2). For comparison, a spectrum of oligomeric poly(n-vinyl butyl ether), which was isolated as a product of radical homopolymerization, is also shown in Fig. 2. The assignment of proton
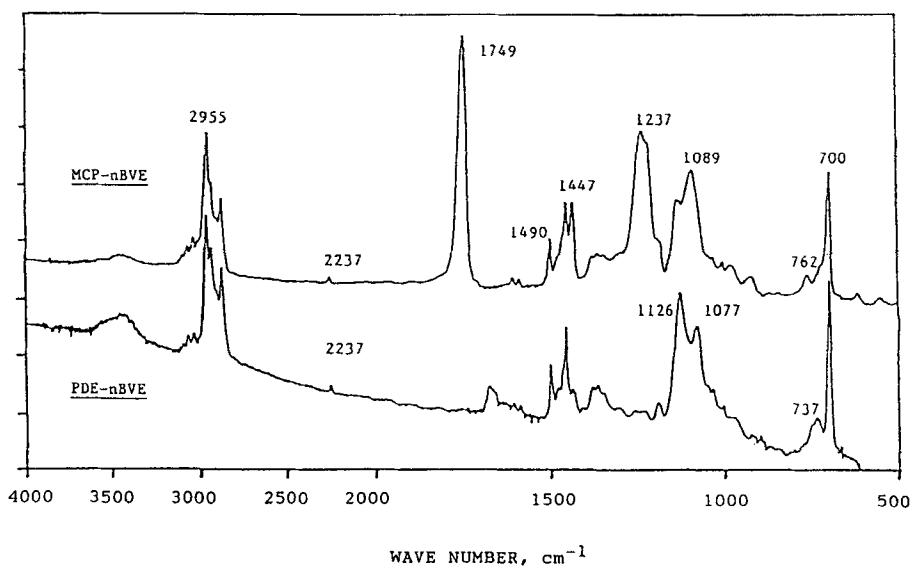
FIG. 1.   FT-IR spectra of MCP and PDE copolymers with nBVE.

resonances for nBVE and other vinyl ether copolymers (Table 1) was carried out based on the spectra of model compounds, monomers, polymers, as well as the results of the peaks' areas integration. The integration data support the equimolar composition of the copolymers.

Similar to the spectra of all studied copolymers, the spectra of MCP–nBVE and PDE–nBVE copolymers have three groups of overlapping peaks which appear in 7.5 to 6.5, 4.5 to 2.3, and 2.3 to 0.5 ppm ranges (Fig. 2). The assignment of the peaks due to the protons of the nBVE monomer unit is presented in Fig. 2, whereas the assignment data for other copolymers is summarized in Table 1.

The peaks in the 2.7 to 3.2 ppm range are assigned to the methine protons of the trisubstituted ethylene monomer units, MCP and PDE, similarly to the assignment of these resonances in the spectra of MCP and PDE copolymers with styrene [7, 10], vinyl acetate [11, 12], and N-vinyl pyrrolidone [13, 14]. A broad peak in the 2.8 to 4.2 ppm range is assigned to the methoxy protons of the MCP monomer unit [10, 11, 13]. All spectra show a broad signal of aromatic protons at 7.5–6.5 ppm, resulting from overlapping multiplets of the five spin system [10].

The composition of the copolymers can be estimated from ^{1}H-NMR spectra using the ratio of peak areas of aromatic protons of a trisubstituted monomer unit and all other protons. For example, the composition of the PDE–nBVE copolymer can be calculated using the relation: $m_1/m_2 = 12S_1/(5S_2 - S_1)$, where m_1 and m_2 are the mole fractions of PDE and nBVE in the copolymer, respectively, S_1 is the area of the peak corresponding to the absorption of the PDE aromatic protons, and S_2 is the peak area of all other protons of PDE and nBVE units. Thus, integration of the peaks in Fig. 2 for PDE–nBVE copolymer gives $S_1 = 328$ and $S_2 = 860$ (arbitrary units). Substitution of these values into the above equation results in equimolar composition of the copolymer ($m_1/m_2 = 0.99$).
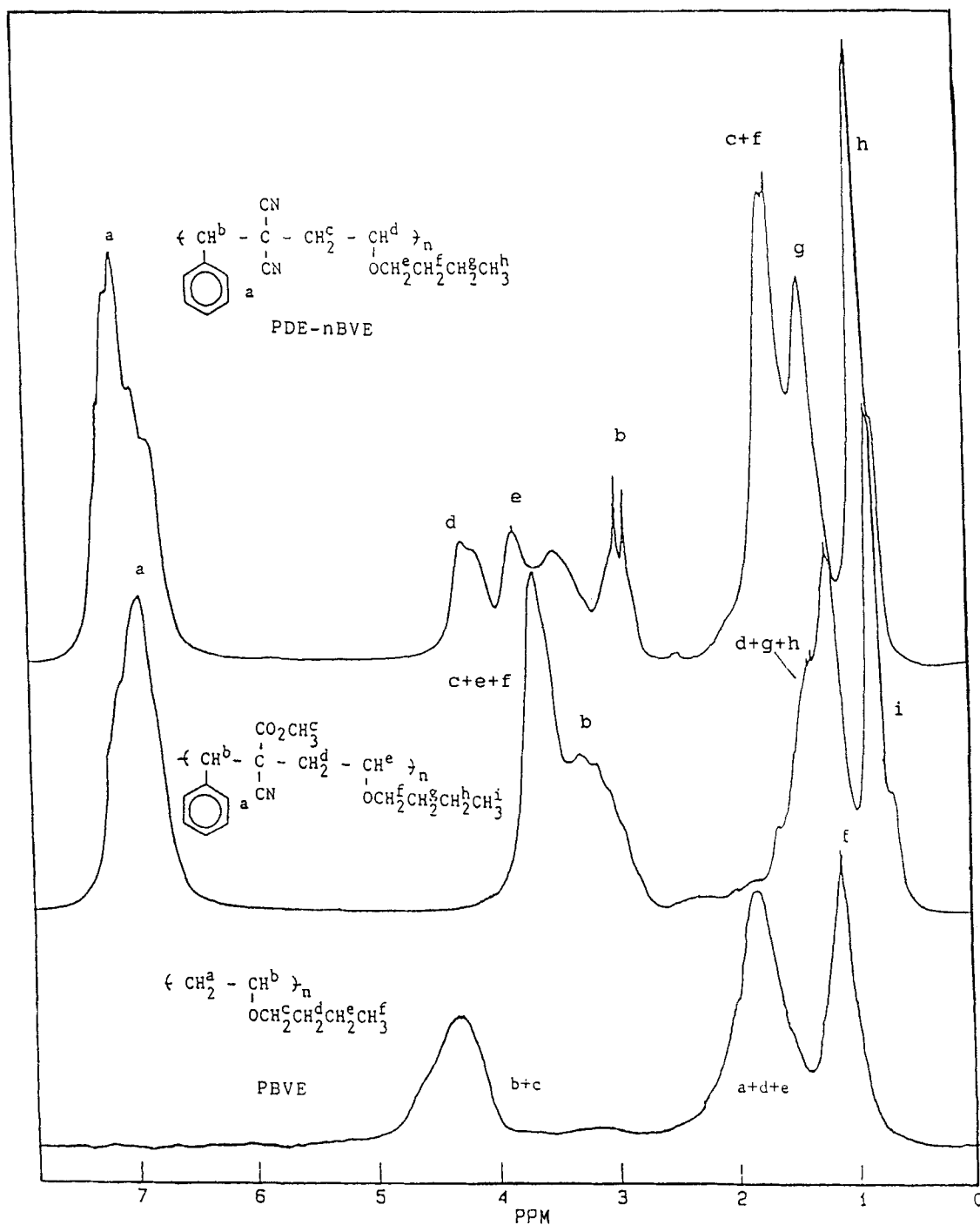
FIG. 2.   ¹H-NMR spectra of MCP and PDE copolymers with nBVE, and poly(n-vinyl ether), PBVE.

TABLE 1. ^{1}H-NMR Chemical Shift Values of Vinyl Ether (CH$_2$=CHOR) Monomer Unit in the MCP and PDE Copolymers

Copolymer	R	Main chain		Chemical shift values, δ (ppm) R			
		CH$_2$	CH	a	b	c	d
MCP–EVE	CH$_2^a$CH$_3^b$	1.0–2.2	2.8–4.2	2.8–4.2	0.5–1.3	—	—
MCP–nBVE	CH$_2^a$CH$_2^b$CH$_2^c$CH$_3^d$	1.0–2.3	2.8–4.5	2.8–3.5	0.5–2.3	0.5–2.2	0.5–1.2
MCP–iBVE	CH$_2^a$CH^b(CH$_3$)$_2$	1.0–2.2	2.5–4.0	2.5–4.0	1.1–2.2	—	—
MCP–CEVE	CH$_2^a$CH$_2^b$Cl	0.8–2.2	2.8–4.2	2.8–4.2	2.8–4.2	—	—
MCP–PVE	C$_6$H$_5^a$	0.8–2.3	4.0–5.2	6.0–7.5	—	—	—
PDE–EVE	CH$_2^a$CH$_3^b$	1.3–1.7	3.8–4.5	3.2–4.2	0.5–1.5	—	—
PDE–nBVE	CH$_2^a$CH$_2^b$CH$_2^c$CH$_3^d$	1.3–1.7	3.8–4.6	3.0–4.2	0.8–2.3	0.7–2.0	0.5–1.2
PDE–iBVE	CH$_2^a$CH^b(CH$_3$)$_2$	1.1–2.3	3.9–4.5	3.2–3.8	1.1–2.2	0.7–1.1	—
PDE–CEVE	CH$_2^a$CH$_2^b$Cl	1.0–2.2	3.9–4.5	3.2–4.0	3.2–4.0	—	—
PDE–PVE	C$_6$H$_5^a$	1.3–2.5	4.9–5.3	6.5–7.5	—	—	—

^{13}C-NMR Spectra

Figures 3 and 4 present tentative assignments of carbon resonances in the 50.3-MHz ^{13}C-NMR spectra for MCP and PDE copolymers with nBVE. The aromatic carbon resonances in the 125 to 140 ppm range are assigned based on the comparison with the spectra of model compounds and polymers. A weaker resonance at a lower field (135 ppm) is assigned to the quaternary phenyl carbon of the PDE or MCP unit. Introduction of more polar vinyl monomer units (i.e., acrylonitrile) in the polystyrene chain results in a shift of the quaternary carbon resonance into the 139 to 142 ppm range [15]. This assignment is supported by the comparison with the ^{13}C-NMR spectra of the PDE monomer, where the quaternary carbon atom absorbs at 134 ppm [16]. Meta- and ortho-aromatic carbon resonances of PDE and MCP apparently contribute to the absorption with maximum at 128–129 ppm. The nitrile carbon resonances are observed in the 111.5 to 117 ppm range. This assignment is consistent with that reported for PDE [16] and for various copolymers containing bis-geminal cyano groups [17].

All backbone carbons of the vinyl ethers, MCP, and PDE have resonance signals in the 30 to 85 ppm range. Methine and methylene carbons of the vinyl ether monomer unit absorb at 75–80 and 35–45 ppm, respectively. The methine carbon resonance of PDE and MCP is observed in the 53 to 58 ppm range for all copolymers, while the quaternary backbone carbon absorption is different for MCP and PDE copolymers, 48–52 and 35–39 ppm, respectively. All assignments for the copolymers are summarized in Table 2.

The DEPT (distortionless enhancement by polarization transfer) NMR technique [18] helps to improve and verify assignments made on the basis of the ^{13}C-NMR spectra by recording methine and methyl resonances as positive and methylene as negative resonances with no quaternary carbon resonance (Figs. 3 and 4). On the other hand, ^{13}C-NMR JMODXH spectra of MCP–nBVE and PDE–nBVE copolymers, presented in Figs. 3 and 4, respectively, give only quaternary carbon resonances and no methine, methylene, or methyl carbons absorptions. This is particularly important for the assignment of the MCP and PDE quaternary carbons which overlap with the vinyl ethers' methylene and MCP methine carbon resonances, respectively, in the conventional ^{13}C-NMR spectra. The spectra also clearly show multiple resonances for quaternary carbons of phenyl rings of PDE and MCP units, as well as cyano carbons. In order to provide additional experimental evidence for the peak assignments, heteronuclear correlated two-dimensional NMR experiments were used to examine the correlation between the carbon and proton resonances. Figures 5 and 6 present the ^{1}H-^{13}C-NMR chemical shift correlated spectra of nBVE copolymers with MCP and PDE, respectively. We found correlation between the MCP and PDE methine proton resonance and the ^{13}C-peak of the methine carbon. Similarly, ^{13}C-resonances of nBVE CH$_2$-carbons (42 and 45 ppm) correlate well with the proton peaks in the 1.0 to 2.2 ppm range. Matching of proton peaks in the 2.8 to 3.8 ppm (MCP) and 3.2 to 4.2 ppm (PDE) ranges with the ^{13}C-peaks at 80 ppm supports the assignment of these absorptions to the vinyl ether methine carbons and protons.

Microstructure

The application of high resolution ^{13}C and ^{1}H NMR, ^{13}C-distortionless enhancement by polarization transfer, 2D ^{13}C-^{1}H-correlated (HETCOR), and 2D
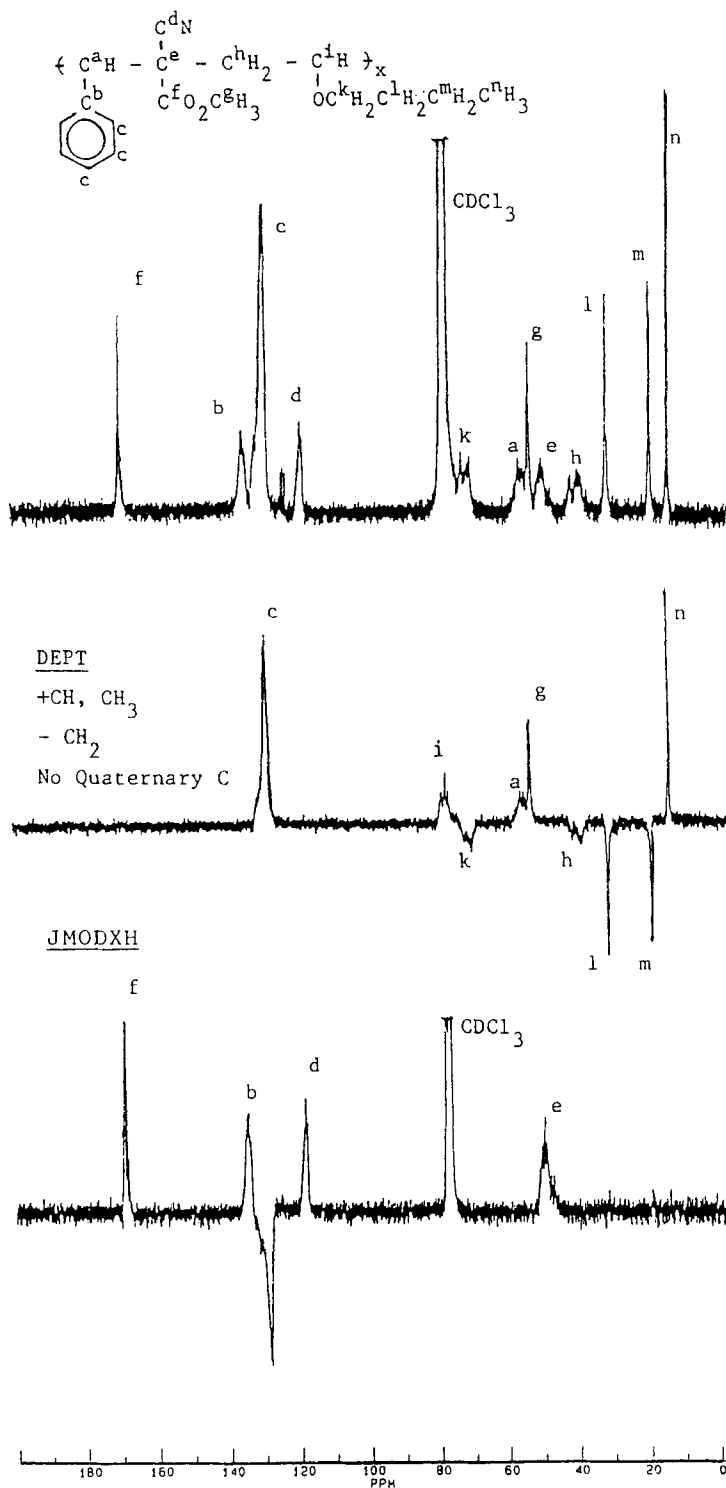
FIG. 3. ¹³C-NMR proton decoupled, DEPT and JMODXH spectra of MCP–nBVE copolymer.

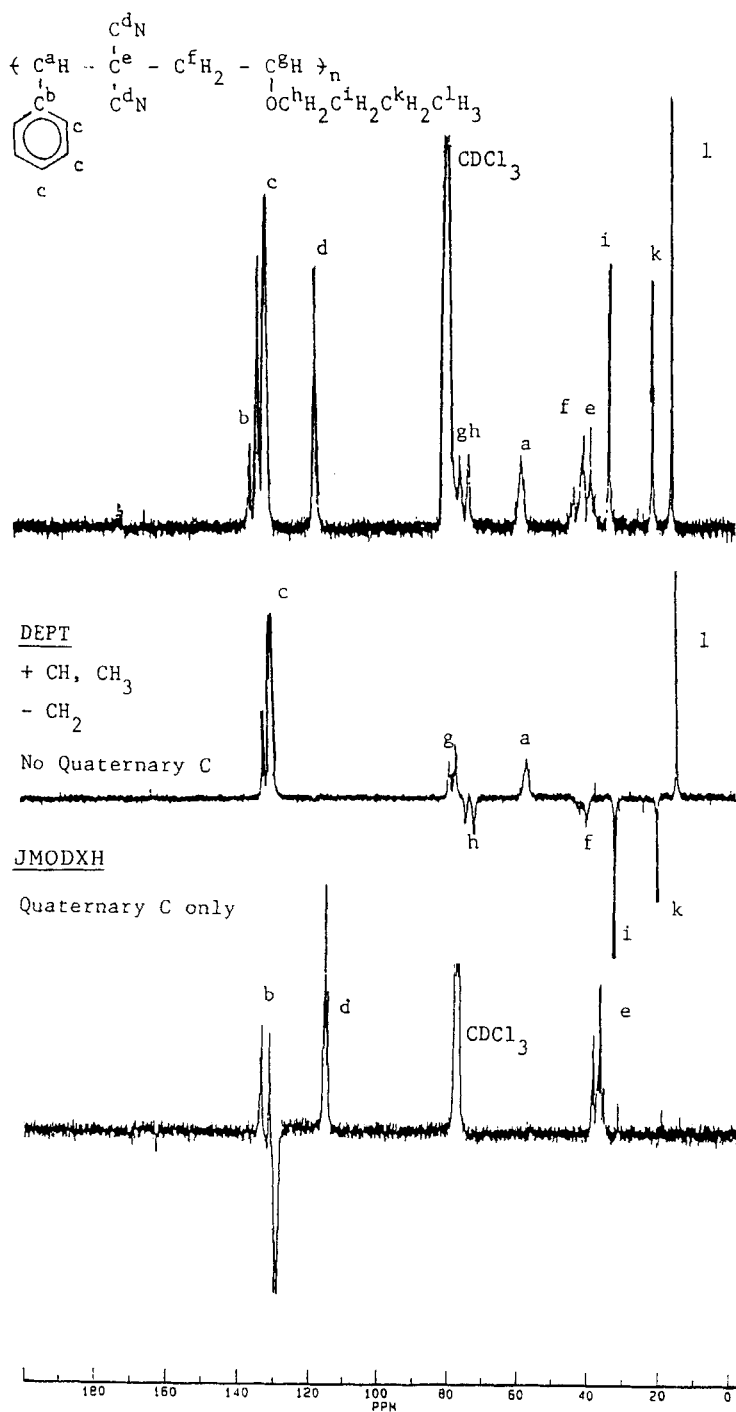FIG. 4. ^{13}C-NMR proton decoupled, DEPT and JMODXH spectra of PDE–nBVE copolymer.

TABLE 2. ^{13}C-NMR Chemical Shift Values of MCP and PDE Copolymers of the Vinyl Ethers

$$-C^1H_2-C^2H-C^3 \underset{\underset{C^5N}{\overset{|}{\underset{OR}{|}}}}{\overset{\overset{C^6OOC^7H_3}{|}}{\underset{}{}}} C^4H- \\ Ph^8$$

R: $-C^9H_2C^{10}H_3$;
$-C^9H_2C^{10}H_2C^{11}H_2C^{12}H_3$
$-C^9H_2C^{10}HC^{11}H_3$
$\quad\quad\overset{|}{C^{12}H_3}$
$-C^9H_2C^{10}H_2Cl$
$-Ph^9$

^{13}C-NMR chemical shift values for Carbons

| Copolymer	1	2	3	4	5	6	7	8	9	10	11	12
MCP-EVE	36–45	75–80	47–52	52–60	118	170	53	126–137	65–70	14	—	—
MCP-nBVE	38–45	75–80	43–52	52–60	118	168	53	127–138	68–75	31	20	13
MCP-iBVE	35–45	79–82	38–43	53–58	118	170	53	125–135	75–79	79	29	19
MCP-CEVE	38–42	76–82	48–52	52–58	118	170	53	127–137	68–73	70	—	—
MCP-PVE	38–44	72–77	45–53	52–58	119	168	54	125–137	116,122	—	—	—
PDE-EVE	38–43	73–80	35–38	55–60	115	—	—	127–137	65–70	15	—	—
PDE-nBVE	37–45	75–81	35–41	55–60	115	—	—	127–134	70–77	31	20	15
PDE-iBVE	38–42	78–80	35–41	54–58	115	—	—	128–137	78–81	75–78	29	20
PDE-CEVE	37–43	75–80	35–43	53–58	115	—	—	128–137	70–75	70–79	—	—
PDE-PVE	35–42	71–75	35–42	52–57	117	—	—	128–137	119,123	—	—	—
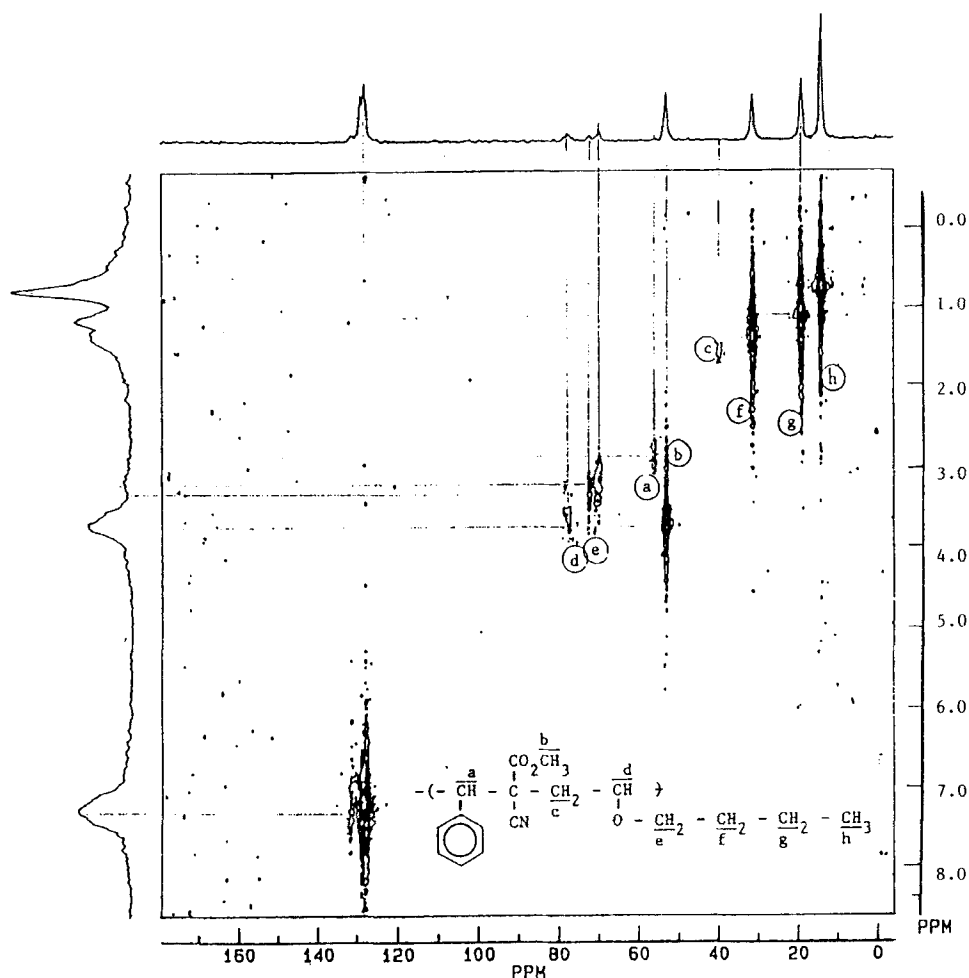
FIG. 5.   Heteronuclear two-dimensional ^1H-^{13}C correlated NMR spectrum of MCP–nBVE copolymer.

^1H-^1H-correlated (NOESY) spectroscopy techniques have been successful in eluci-dating skeletal arrangement of monomer units [19]. These techniques were utilized in the microstructure analysis of the equimolar alternating copolymer of PDE and PVE, which has a well-resolved ^1H-NMR spectrum (Fig. 7A). In this case there is no overlap of the methine and methylene backbone resonances with those of the alkoxy groups, in contrast to the spectra of other copolymers of vinyl ethers with MCP and PDE (Fig. 2 and Table 1). The ^1H-NMR spectrum in Fig. 7A shows an unresolved peak of the PVE methine proton and better resolved peaks of the PDE methine (2.8–3.5 ppm) and PVE methylene protons (1.1–2.6 ppm). Assignment of these ranges is based on the ^1H-^{13}C 2D correlation diagram similar to that presented in Fig. 6. The 2D ^1H-^1H-correlation spectroscopy (NOESY) provides information about spin-spin coupling between protons. The NOESY spectrum in Fig. 7B shows
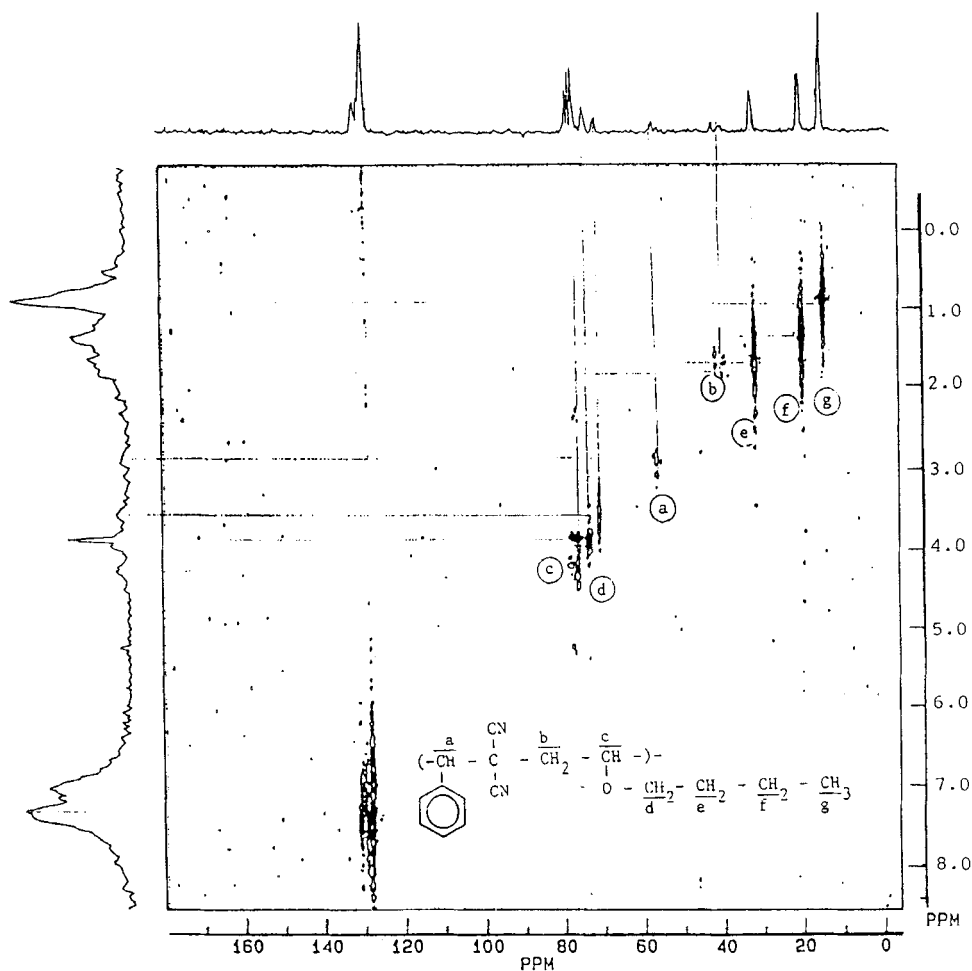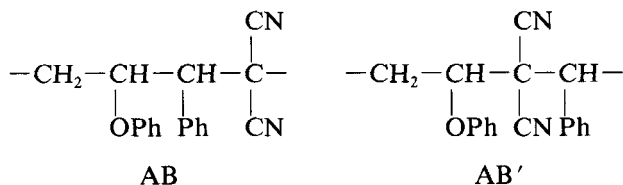
FIG. 6.   Heteronuclear two-dimensional ^{1}H-^{13}C correlated NMR spectrum of PDE–nBVE copolymer.

correlation between PVE methine protons at 5.2 ppm and PDE methine protons at 3.0 ppm. It indicates the existence of a regiospecific arrangement for the PDE–PVE

$$-CH_2-\underset{OPh}{CH}-\underset{Ph}{CH}-\underset{CN}{\overset{CN}{C}}- \qquad -CH_2-\underset{OPh}{CH}-\underset{CN}{\overset{CN}{C}}-\underset{Ph}{CH}-$$

                     AB   AB'

dyads where the PVE methine carbon is connected with the PDE methine carbon (AB dyad). PVE methylene protons (1.8 ppm), on the other hand, correlate not only with the PVE methine proton at 5.2 ppm but also with the methine proton of
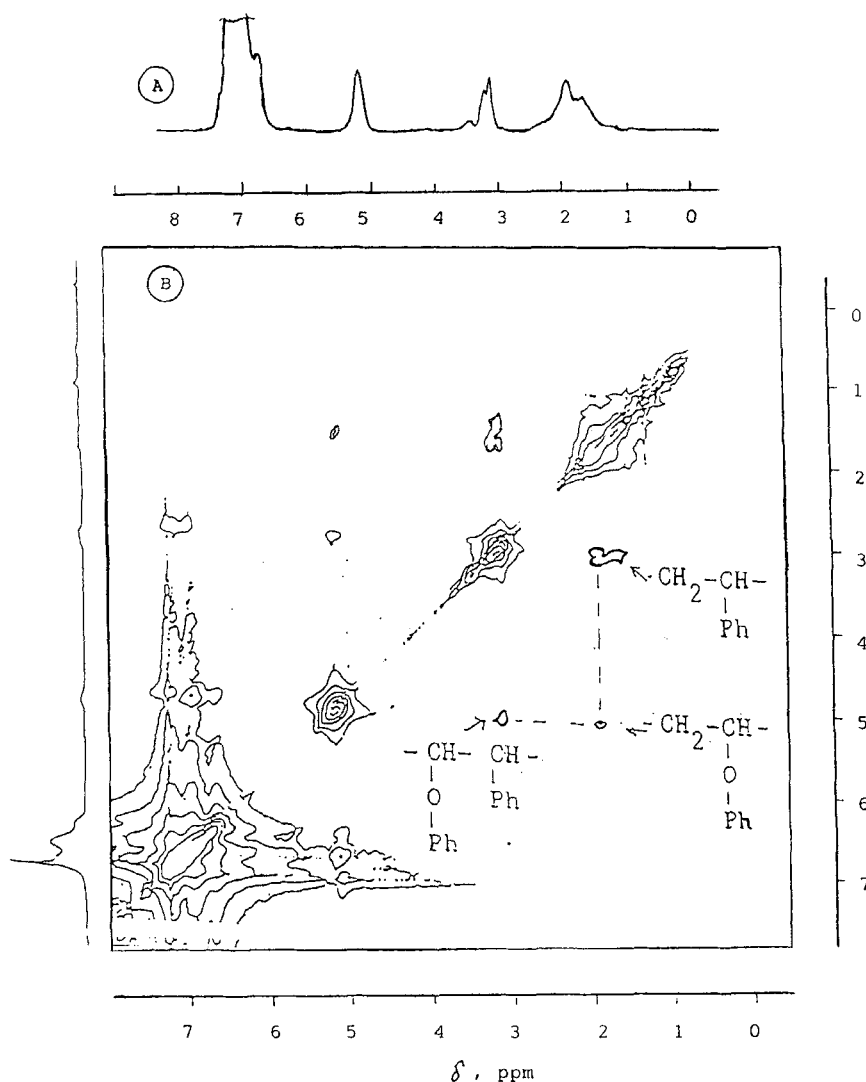
FIG. 7. ^{1}H (A) and homonuclear two-dimensional ^{1}H-^{1}H correlated (B) NMR spectra of PDE–PVE copolymer.

the PDE unit at 3.3 ppm. This observation suggests that some PDE–PVE alternating dyads have the AB′ structure, where the PVE methylene group is attached to the PDE methine group. Both regiospecific structures were inferred from the NMR data for styrene copolymers with MCP [10] and PDE [7]. The methine proton of the PVE monomer unit does not appear to be sensitive to the copolymer stereochemistry as much as other backbone protons, probably because, in both dyads, it is in the proximity of the deshielding groups, either phenylmethylene (AB) or dicyanomethylene (AB′). It is reasonable to assume that the splitting observed for the PDE methine proton (Fig. 7A) reflects a shielding/deshielding environment for this

proton. The low-field peak of the PDE methine resonance at 3.4 ppm is assigned to the PDE unit in the AB dyad due to the proximity of the deshielding phenyloxymethylene group, while the high-field resonance at 3.1 ppm corresponds to the PDE unit in the AB′ dyad.

Multiple peaks of the PDE methine and PVE methylene protons most likely arise due to the different orientations of the alternating monomer units rather than the tacticity of the alternating dyads. Free-radically initiated polymers are usually typically predominantly atactic (with a slight preference for the syndiotactic placement) [20], which leads to the relative broadness of the peaks. The sensitivity of the chemical shifts to different stereochemical environments usually decreases rapidly with distance. It can be assumed, therefore, that a given proton in an alternating copolymer is most sensitive to the atoms and groups located one or two bonds away rather than to the effects of iso- or syndio-placement of the alternating monomer units.

The splitting of the PVE methylene resonance into four components (Fig. 7A) apparently reflects the triad sensitivity of these protons. Assuming a very low probability of PDE and PVE homopropagation, which can be inferred from the independence of the copolymer composition (equimolar) of the comonomer feed, there are four possible structures of the PVE-centered triads.
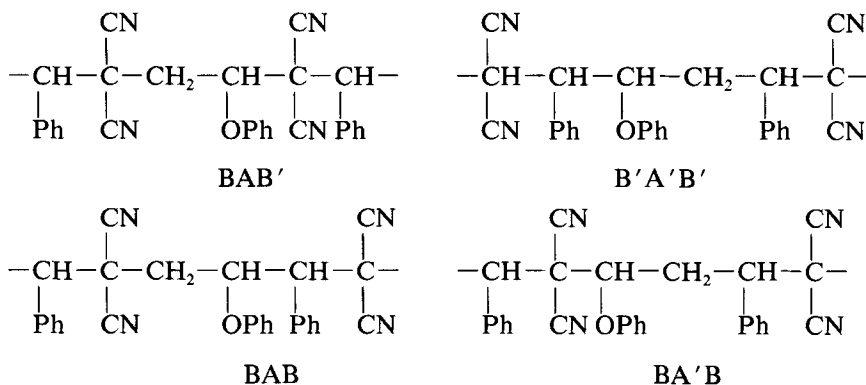
The four components of the methylene resonance are tentatively assigned according to the influence of deshielding groups located one and two bonds away. This resonance should move into the lower field with the proximity of the neighboring deshielding dicyanomethylene and phenylmethylene groups of PDE units. The methylene resonances should increase (in δ scale) in the triad sequence: BAB′ > BAB > BA′B > B′A′B′. The low field component (a shoulder at 2.2 ppm) of the overlapping peaks in the 1.3 to 2.5 ppm range is, therefore, assigned to methylene protons in the BAB′ triads, a major peak at 1.9 ppm to the BAB triad, a peak at 1.7 ppm to the BA′B triad, and a peak at 1.6 ppm to the B′A′B′ triad. Resonances of PVE methylene protons are shifted to lower fields due to deshielding which conceivably arises from a powerful electron withdrawal effected by neighboring cyano groups. Similar low field shifts for both PVE methylene and methine protons were observed in the case of PVE alternating copolymers with tetracyanoquinodimethane [21].

The approximate area ratio of the low field absorption and the high-field peaks is 0.17:0.83. This is about the same for the PDE methine proton and PVE methylene protons absorptions, and thus indicates a predominance of PDE-PVE dyads and triads, where PVE methylene carbon is connected with PDE methine carbon.

Thermal Properties

The copolymers of MCP and PDE with the vinyl ethers are amorphous and show no crystalline DSC endotherms. This behavior is similar to that of the copolymers of these trisubstituted ethylenes with styrene [22], vinyl acetate [11, 12], and N-vinyl pyrrolidone [13, 14]. The glass transition temperatures of the MCP copolymers with vinyl ethers are higher than those of the PDE copolymers (Table 3). It is apparently associated with the presence of a bulkier carbomethoxy group in MCP instead of the cyano group. The DSC analysis of vinyl acetate copolymers of MCP and PDE of comparable composition also show a higher T_g of the MCP copolymer (170°C) than that of the PDE copolymer (144°C). The order of decreasing T_g (EVE > PVE > CEVE > iBVE > nBVE) is the same for both MCP and PDE copolymers with vinyl ethers. In the series EVE > iBVE > nBVE, T_g values are lowered with increasing side-chain length, thereby increasing the free volume and, hence, the chain mobility. Branching increases the size of the group, which results in higher T_g values for iBVE compared with the T_g of nBVE-based copolymers. These T_g values are consistent with a trend found for a series of poly(alkyl acrylates) [23], polyvinyl ethers [24], and copolymers of maleic anhydride with alkyl vinyl ethers [25].

Information on the degradation of the copolymers was obtained from thermogravimetric analysis. The decomposition products were not analyzed in this study, and the mechanism has yet to be investigated. Results of the analysis are summarized in Table 3. TGA curves for EVE and CEVE copolymers with MCP and PDE (Fig. 8) show typical degradation patterns of MCP- and PDE-based copolymers with vinyl monomers. Decomposition of all copolymers on air occurred in two distinct stages, rapidly in the 220 to 350°C region, then more slowly at 350–700°C. The formation of a thermally stable carbon residue upon decomposition of CEVE copolymers apparently is associated with crosslinking. As dehydrochlorination reac-

TABLE 3.   Thermal Properties of MCP and PDE Copolymers with the Vinyl Ethers

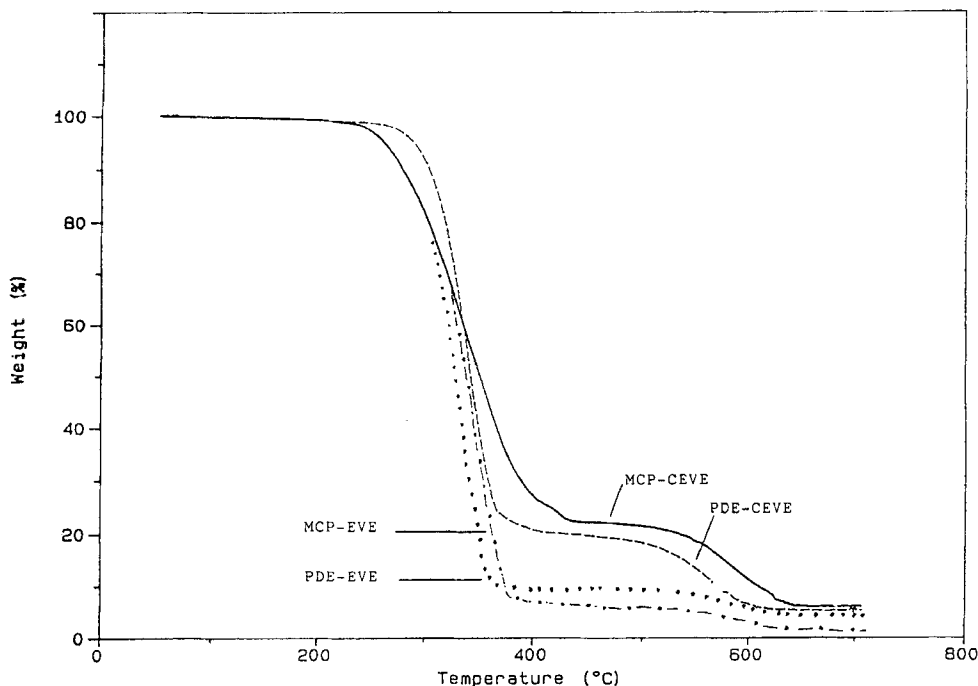| Copolymer	T_g, °C	Temperatures at decomposition, °C			
		Onset	10%	50%	90%
MCP–EVE	158	242	276	336	374
MCP–nBVE	124	220	292	337	369
MCP–iBVE	130	260	254	339	403
MCP–CEVE	142	246	279	351	606
MCP–PVE	152	248	268	340	450
PDE–EVE	152	230	280	326	371
PDE–nBVE	114	220	306	336	374
PDE–iBVE	120	250	290	326	360
PDE–CEVE	135	275	303	342	565
PDE–PVE	147	262	280	340	456

FIG. 8.   Results of TG analysis of MCP and PDE copolymers with EVE and CEVE.

tion proceeds, particularly at higher temperature, the abstraction of a hydrogen atom from an adjacent chain results in crosslinking structure [26].

CONCLUSIONS

Copolymerization of MCP and PDE with ethyl, *n*-butyl, *i*-butyl, 2-chloroethyl, and phenyl vinyl ethers in broad ranges of comonomer ratios always produces copolymers of an equimolar composition. Microstructure analysis of the copolymer of PDE and phenyl vinyl ether, as deduced from ^{1}H and NOESY ^{13}C-NMR data, demonstrated the formation of alternating monomer structures with different orientation of the monomer units. The order of decreasing T_g values, ethyl > phenyl > 2-chloroethyl > *i*-butyl > *n*-butyl vinyl ether (the same for MCP and PDE), correlates well with the structure of the alkoxy group.

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