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Polymerization and copolymerization of dimethyl(1-ethoxycarbonyl)vinyl phosphate

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Abstract

Dimethyl(1-ethoxycarbonyl)vinyl phosphate (DMEVP), prepared in nearly quantitative yield from the reaction of ethyl bromopyruvate with trimethyl phosphite, polymerizes easily by free radical initiated polymerization and copolymerizes readily with styrene (S). Reactivity ratios determined at 60 and 135 °C were $r_S = 0.21 \pm 0.02$, $r_{DMEVP} = 0.35 \pm 0.05$ and $r_S = 0.31 \pm 0.03$, $r_{DMEVP} = 0.31 \pm 0.04$, respectively. Glass transition temperatures and thermal stabilities of the copolymers decreased but char yields obtained upon thermolysis increased as the DMEVP contents of the copolymers increased. ^{1}H, ^{13}C and ^{31}P NMR spectra of the copolymers are reported. DMEVP exhibited mild chain transfer activity ($C_{tr} \sim 0.01$) in styrene polymerizations conducted at 135 °C and in emulsion polymerizations at 50 °C.

Keywords: Organophosphorus; Monomer; Copolymer

1. Introduction

Much information has been accumulated about the polymerization and copolymerization behavior of α-substituted acrylates [1–3]. Such monomers have large steric requirements when incorporated in or at the ends of growing polymer chains and this can be manifested in many ways. In some cases, the ceiling temperatures for polymerization of the monomers may be very low and the monomers may not even be homo-polymerizable. In other cases, the rates of termination reactions may be sufficiently low relative to the rates of propagation reactions, that ‘steric assisted polymerization’ occurs [4–8]. In yet other instances, steric strain at a propagating polymer radical site may be relieved by fragmentation so that the phenomenon of chain transfer by addition/fragmentation is observed [9–18].

Not much information is available regarding the polymerization characteristics of vinyl monomers with α-phosphate, α-phosphonate or α-phosphinate substituents. Patents by Coover, et al. claim polymerizations of vinyl monomers containing phosphonate and phosphonodiamidate substituents [19,20] but Muray noted that diethyl α-phenylvinyl phosphate failed to polymerize [21] while Jin and co-workers reported that this monomer does not copolymerize well with acrylonitrile although it forms an alternating copolymer with maleic anhydride [22]. Alexandratos, et al. reported that the tetraethyl ester of vinylidenediphosphonic acid, Et$_4$VDPA, fails to polymerize but copolymerizes well with divinylbenzene to form crosslinked products with high Et$_4$VDPA contents [23]. Willersinn and Distler describe polymerization and copolymerization reactions of several 1-alkoxycarbonylvinyl phosphate esters and use of the products as plasticizers and combustion-resistant materials [24]. However, no detailed studies on the polymerization characteristics of monomers of this general type have appeared.

In this paper, we report on the polymerization and copolymerization behavior of an acrylate ester that is substituted in its α-position by a phosphate radical. Such monomers are easily synthesized by the Perkow reaction [25,26], and are of interest because they can provide a means to incorporate phosphorus-containing groups into vinyl polymers and because they also have the potential of being addition/fragmentation chain transfer agents [27,28].

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2. Experimental

2.1. Monomer synthesis

Dimethyl(1-ethoxycarbonyl)vinyl phosphate (DMEVP), was synthesized in a manner similar to that described by Barton et al. [29]. Trimethyl phosphite (3.10 g, 0.025 mol) was added dropwise to a stirred solution of ethyl bromopyruvate (4.88 g, 0.025 mol) in chloroform (5 ml) at 0 °C under argon. The mixture was stirred at room temperature for 3 h and then distilled at 70 °C (9 mm Hg) to obtain 5.5 g (98%) of product. ^{1}H NMR (δ (ppm), TMS ref., $CDCl_3$) 1.30 (t, $J = 7.1$ Hz), 3.85 (d, $J = 11.7$ Hz), 4.25 (q, $J = 7.2$ Hz), 5.59 (t, $J = 2.4$ Hz), 5.95 (t, $J = 2.1$ Hz); ^{13}C NMR (δ (ppm), TMS ref., $CDCl_3$) 13.8, 54.9, 61.8, 110.8, 143.6, 161.6; ^{31}P NMR (δ (ppm), 85% H_3PO_4 ref., $CDCl_3$) -3.7.

2.2. Polymerization and copolymerization

Polymerizations and copolymerizations were conducted in bulk or emulsion systems. Bulk polymerization experiments were performed at 60 and 135 °C. Experiments conducted at 60 °C employed 0.1 mol% AIBN as initiator and lasted 2 h. Experiments conducted at 135 °C were conducted without added initiator and lasted 30 and 60 min. The reaction mixtures were poured into methanol to precipitate the polymers. These were collected and purified by reprecipitation from benzene solution into methanol and then dried under vacuum at 40 °C overnight.

Emulsion polymerization experiments were conducted at 50 °C for 4 h using potassium persulfate as the initiator. Typical recipes consisted of 10.0 g distilled water, 1.2 g sodium dodecyl sulfate, 2.0 g monomers and 0.05 g initiator. The conversions were more than 90% in all cases. The polymerization mixtures were poured into methanol to precipitate the polymers. These were purified by reprecipitation from benzene solution into methanol and then dried at 40 °C under vacuum overnight.

2.3. Molecular weight measurements

Molecular weight characterization was done using a Waters GPC apparatus equipped with three Styragel® columns (HR1, HR4E and HR5E). Samples of the polymers in THF (0.18% w/v) were passed through the column set at 1.0 ml/min and 35 °C and the eluant analyzed by refractive index, light scattering and viscosity detectors. TriSEC software (version 3.00) was used to process the data.

2.4. NMR measurements

^{1}H NMR spectra of samples in $CDCl_3$ solution were recorded using a Varian Mercury 300 MHz NMR Spectrometer and TMS as an internal standard. ^{31}P NMR spectra of samples in $CDCl_3$ were recorded at 121.4 MHz using an INOVA 500 spectrometer, 85% *ortho*-H_3PO_4 as an external standard, continuous WALTZ-modulated ^{1}H-decoupling, a pulse angle of 45° and an acquisition time of 1.6 s. ^{13}C NMR spectra of samples in $CDCl_3$ were recorded at 125 MHz using an INOVA 500 spectrometer, a 90 degree pulse, a pulse delay of 5 s and an acquisition time of 1.8 s. Gated WALTZ-modified decoupling of proton-resonances was employed.

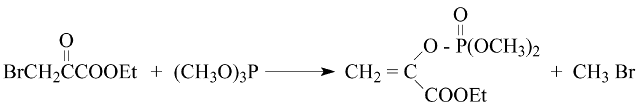
2.5. Thermal measurements

Thermogravimetric measurements were made using a Universal VI.10B Thermal Analysis Instrument and a heating rate of 10 °C/min.

Differential Scanning Calorimetric measurements were also made using the Universal VI.10B Thermal Analyzer and used to determine glass transition temperatures of the polymers. The sample size was 1–13 mg and the heating rate was 10 °C/min. For each sample, two runs were performed and only the second run was analyzed. The glass transition temperature, T_g, was identified as the midpoint of the step transition in the heat flow vs. temperature thermogram.

3. Results and discussion

DMEVP, was easily synthesized in nearly quantitative yield from the reaction of trimethyl phosphite and ethyl bromopyruvate [29].



$$BrCH_2\overset{\overset{O}{\|}}{C}COOEt + (CH_3O)_3P \longrightarrow CH_2{=}C\begin{matrix}O\text{-}\overset{\overset{O}{\|}}{P}(OCH_3)_2\\ COOEt\end{matrix} + CH_3Br$$

1

This material readily polymerized on storage and it copolymerized easily with styrene. Table 1 provides

Table 1
Copolymerization of dimethyl(1-ethoxycarbonyl)vinyl phosphate with styrene at 60 °C

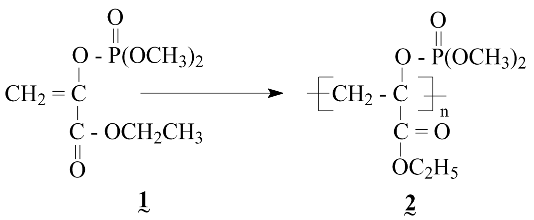
Molar percentage styrene			Conversion (wt%)	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$
Monomer mixture	Copolymer				
	Observed	Calculated[a]			
100	100	–	6.2	132	196
95	83.5	83.9	7.3	117	186
90	75.9	74.4	5.1	141	207
80	62.2	63.1	4.9	149	221
70	57.2	56.4	5.2	167	255
50	44.6	47.2	7.2	201	302
20	31.5	30.2	–	395	458
0	0	–	5.0	–	

0.1 mol% AIBN, 2 h, bulk.

[a] Calculated from monomer feed composition, conversion and reactivity ratios of 0.21 and 0.35 for styrene and DMEVP, respectively.

information about polymerization and copolymerization experiments that were conducted at 60 °C in bulk using 0.1 mol% AIBN as initiator. Based on GPC measurements that will be discussed later in this paper, the polymer appears to have a very high molecular weight.

The ^{1}H NMR spectrum of the polymer obtained (Fig. 1(A)) indicates that conventional polymerization occurs. Thus, it contains four major resonance areas attributable to backbone methylene protons ($\delta = 2.8-3.4$ ppm, relative area = 1.9), protons of the ethyl group ($\delta = 1.2-1.4$ and 4.0–4.3 ppm, relative area = 5.0) and methoxy protons ($\delta = 3.6-3.8$ ppm, relative area = 5.6) of polymer. In addition, the ^{13}C NMR spectrum of the polymer (Fig. 2(D)) contains resonances of C-methyl, O-methyl, O–CH_2, quaternary, backbone-CH_2 and carbonyl carbons at 13.5, 54.2, 62, 84, 46 and 169 ppm, having relative intensities of approximately 1, 2, 1, 1, 1 and 1, respectively.



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The ^{31}P-spectrum of the polymer consisted primarily of a single resonance at −4 ppm (relative to H_3PO_4) which has nearly the same chemical shift as the monomer (−3.7 ppm), with trace signals being detected at ~0.2 and ~11 ppm.

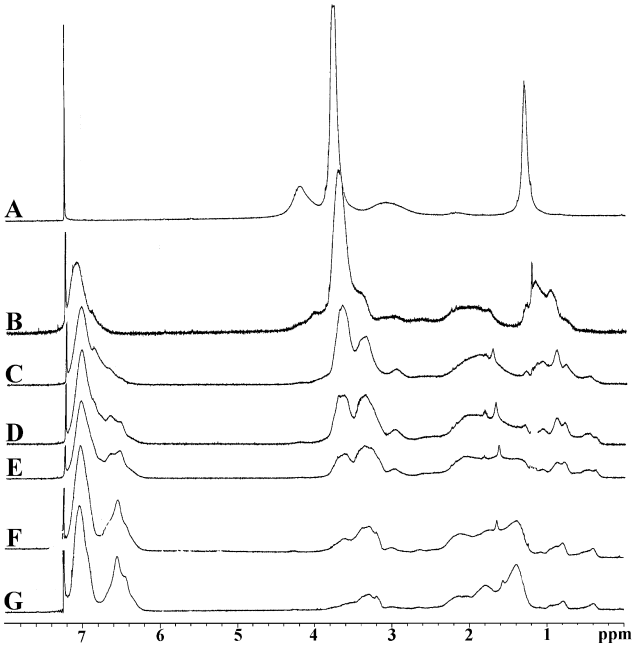

Fig. 1. ^{1}H NMR spectra of polyDMEVP (A) and of DMEVP–styrene copolymers containing 31.5 (B), 44.6 (C), 57.2 (D), 62.2 (E), 75.9 (F) and 83.5 (G) mol% styrene. Weak resonances due to impurities in the 1.2–1.3 and 3.4–3.5 ppm regions have been removed.

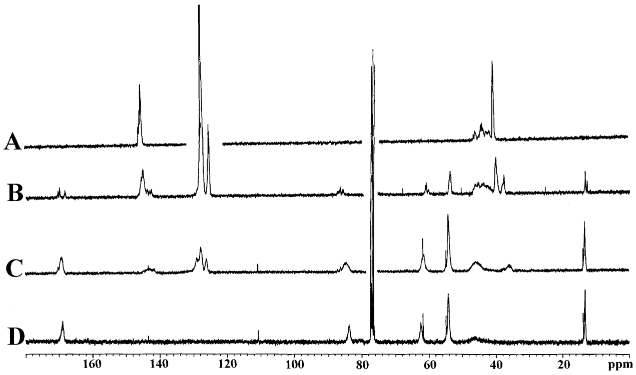

Fig. 2. ^{13}C NMR spectra of polystyrene (partial) (A), of DMEVP–styrene copolymers containing 79 (B) and 32 (C) mol% styrene and of polyDMEVP (D).

3.1. Copolymerization studies

DMEVP copolymerized easily with styrene in bulk at 60 and 135 °C and under emulsion conditions at 50 °C. Tables 1–3 list the data obtained in copolymerization experiments and some of the properties of the copolymers obtained. Differences are noted between the bulk and emulsion copolymerization systems. It seems that DMEVP is more easily incorporated in copolymers in the bulk copolymerization systems and that DMEVP has less of an influence on Mn in bulk systems than in emulsion systems. The tendency of Mn to pass through a minimum as the amount of DMEVP employed is increased is also worth noting.

Figs. 1(B)–(E) and 2(B),(C) show ^{1}H and ^{13}C NMR spectra of the copolymers. The ^{1}H-spectra clearly indicates that copolymers are formed. The CH_3 resonance of ethyl groups appears in multiple places at high field (> 1 ppm) in copolymers with high styrene contents but occurs in a single area centered at 1.15 ppm in the spectrum of the homopolymer. Diamagnetic shielding by neighboring styrene units is believed responsible for the upfield shifts of these resonances in the copolymers. Also, the *ortho* proton resonance of the styrene units changes from the characteristic 3-peak pattern in polystyrene to appear in the same region as the meta and para proton resonances in the spectra of copolymers with low styrene contents. This indicates that the styrene units become flanked by DMEVP units during copolymerization. The compositions of the copolymers were calculated from the relative areas of the aromatic and proton resonance, using the following formula, where A_{Ar} and $A_{\mathrm{CH_3}}$ are the relative resonance areas attributed to aromatic ($\delta = 6.2-7.2$ ppm) and methyl ($\delta = 0.2-1.2$ ppm) protons and are listed in Tables 1–3.

$$\mathrm{Mol\%Styrene} = \frac{300A_{\mathrm{Ar}}/A_{\mathrm{CH_3}}}{5 + 3\mathrm{A}_{\mathrm{Ar}}/\mathrm{A}_{\mathrm{CH_3}}}$$

The ^{13}C NMR spectra of the copolymers were not investigated extensively, but the results obtained qualitatively indicate that their methine carbon resonance patterns can be used to characterize styrene-centered triad distributions.

Table 2
Copolymerization of dimethyl(1-ethoxycarbonyl)vinyl phosphate with styrene at 135 °C

Molar percentage styrene			Conversion (wt%)	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	T_g (°C)
Monomer mixture	Copolymer					
	Observed	Calculated[a]				
100	100	–	22.6	194	322	105
90	79.0	80.9	27.6	97	172	100
80	69.5	68.7	22.8	97	153	89
70	62.8	61.0	21.9	101	159	85
51	49.3	50.5	21.8	122	172	79
20	31.8	31.7	13.1	468	531	71–49
0	0	–	9.4	–		50

30 min thermal reaction in bulk under N_2.

[a] Calculated from monomer feed composition, conversion and reactivity ratios of 0.31 and 0.31 for styrene and DMEVP, respectively.

Thus, in the ^{13}C NMR spectrum of polystyrene, methine carbon resonance is noted at 40 ppm while a copolymer prepared from a 90–10 S/DMEVP mixture (27.6 wt% conversion) exhibits resonances at 40, 38, and perhaps also at 36 ppm, the relative intensities of which are in good visual accord with those expected for S-S-S, (S-S-DMEVP + DMEVP-S-S) and DMEVP-S-DMEVP triads (i.e. relative amounts of 0.62, 0.33 and 0.04, respectively) based on sequence distribution calculations [30]. In addition, a copolymer prepared from a 20/80 S-DMEVP mixture in 31.8 percent conversion contains methine carbon resonances at 38 and 36 ppm having relative intensities in acceptable visual agreement with the relative proportions of styrene units calculated to be centered in (S-S-DMEVP + DMEVP-S-S) and DMEVP-S-DMEVP triads (i.e. a 14:86 ratio).

The ^{31}P NMR resonances of the copolymers occurred at approximately −4 ppm, relative to external H_3PO_4, in all cases and were not useful for microstructure studies.

3.2. Reactivity ratio determinations

The results provided in Tables 1 and 2 were analyzed using the Mortimer–Tidwell program [31] to obtain reactivity ratios for styrene–DMEVP copolymerization at 60 and 135 °C. The values obtained are given in Table 4.

Table 3
Copolymerization of dimethyl(1-ethoxycarbonyl)vinyl phosphate with styrene under emulsion conditions

Molar percentage styrene		Conversion (wt%)	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$
Monomer mixture	Copolymer			
100	100	90.5	520	2,882
99.5	99.7	91.9	210	1,685
98.9	–	89.6	165	1,452
96.8	–	92.4	257	927
94.7	96.4	90.3	180	581
88.7	91.5	92.4	109	304

50 °C, 4 h, 2.0 g monomers, 0.05 g $K_2S_2O_8$, 10 g H_2O, 1.2 g sodium dodecyl sulfate.

Tables 1 and 2 show that copolymer compositions calculated from monomer feed compositions, conversions and these reactivity ratios are in good agreement with those measured for the copolymers. Figs. 3 and 4 show joint confidence limit plots for these reactivity ratios that are based on the Mortimer–Tidwell calculations.

The small values of the reactivity ratios and the reactivity ratio products indicate a strong tendency of styrene and DMEVP to copolymerize. The reactivity ratios are similar to those reported by Yamada and co-workers for the styrene-ethyl α-benzyloxymethyl acrylate copolymerization system [6] and they indicate a tendency for alternation that is higher than that indicated for copolymerizations of styrene with other α-substituted acrylate esters [32,33]. This indicates that the styrene–DMEVP and related copolymerization systems should be useful for preparing polymers with valuable properties, especially combustion resistance.

3.3. Molecular weights

Tables 1–3 list number ($\bar{M}n$) and weight average ($\bar{M}_w$) molecular weights measured for the polymers and copolymers. The $\bar{M}_w/\bar{M}_n$ ratios are close to 1.5 for most of the copolymers prepared in bulk at low conversion but are as high as 6–8 for polymers prepared in high conversion by emulsion polymerization. Surprisingly, molecular weights seem to pass through a minimum as the proportion of DMEVP present in the copolymerization mixture increases. One explanation that may be advanced for this is that steric-assisted polymerization becomes increasingly important as the proportion of DMEVP in the polymerization mixture increases. This would become particularly significant at

Table 4
Reactivity ratios determined for styrene–DMEVP copolymerization

Polymerization temperature (°C)	r_S	r_{DMEVP}	$r_S \cdot r_{DMEVP}$
60	0.21 ± 0.02	0.35 ± 0.05	0.08
135	0.31 ± 0.03	0.31 ± 0.04	0.09

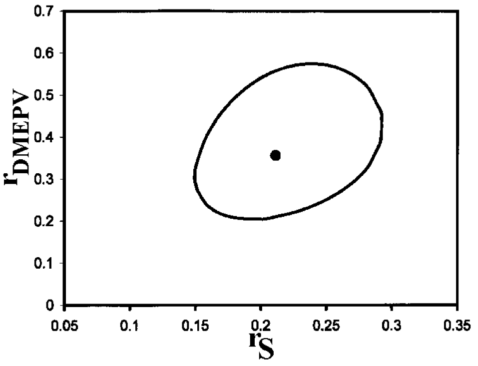

Fig. 3. Reactivity ratio 15% joint confidence limits for copolymerization of DMEVP with styrene at 60 °C.

high DMEVP levels and that indeed seems to be the case. The initial fall in molecular weight with DMEVP level may be due to chain transfer by addition/fragmentation that is also possible with DMEVP.

The copolymers obtained by emulsion polymerization had very high molecular weight distributions that tended to narrow as the DMEVP levels increased. This again could indicate the occurrence of chain transfer by addition/fragmentation to some extent.

3.4. Thermal properties of the copolymers

DSC and TGA measurements were conducted on the copolymers prepared at 135 °C. Except for one sample (31.8 mol% styrene) which exhibited two transitions, all the samples exhibited changes in heat flow vs. temperature curves that could be identified with glass transition temperatures. The values obtained are listed in Table 2.

According to Fox [34], the glass transition temperatures of many copolymers, T_g, obey the following equation, where W_A is the weight fraction of one of the monomers (A) present, $T_{g,A}$ is the glass transition temperature (in degrees Kelvin) of its homopolymer, and $T_{g,B}$ is the glass transition temperature of the homopolymer of the other monomer (B).

$$\frac{1}{T_{g,cop}} = \frac{W_A}{T_{g,A}} + \frac{(1-W_A)}{T_{g,B}} \tag{1}$$

Accordingly, plots of $1/T_{g,cop}$ versus W_A are often linear. However, Johnston and others [35] have noted that positive and negative deviations from this linear relationship may occur and that in such cases, the glass transition temperatures of copolymers can be related to those of the corresponding homopolymers and that of the perfectly alternating copolymer ($T_{g,Alt}$) by the following equation which also includes conditional probabilities (P(A/A), P(B/A), P(A/B) and P(B/B)) for monomer placements in the copolymers.

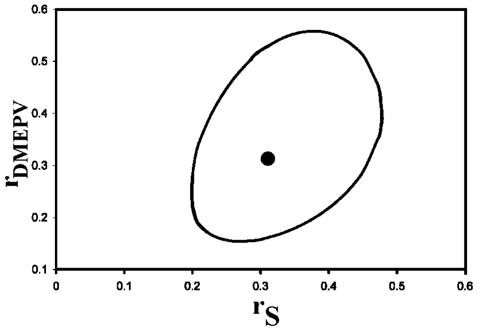

Fig. 4. Reactivity ratio 95% joint confidence limits for DMEVP–styrene copolymerization at 135 °C.

$$\frac{1}{T_{g,cop}} = \frac{1}{T_{g,A}} W_A P(A/A) + \frac{1}{T_{g,Alt}} \Big(W_A P(B/A) + (1-W_A) P(A/B) + \frac{1}{T_{g,B}} (1-W) P(B/B) \Big) \tag{2}$$

Fig. 5 shows a plot of $1/T_{g,cop}$ vs. the weight fraction of styrene in the copolymers. The plot is clearly not linear, indicating that the Fox equation (Eq. 1) is not appropriate for the copolymers; their glass transition temperatures are higher than this equation would predict. However, the data are nicely fit by Eq. 2 given above, assuming a T_g value for the alternating copolymer of 85 °C. This is ten degrees higher than what would be expected for an equimolar copolymer assuming the Fox equation. This interesting result suggests that there are substantial steric interactions between styrene and DMEVP units at monomer sequence junctions in the copolymers. It also suggests that, with appropriate monomer variations, similar phosphorus-containing copolymers having softening points in a useful range may be obtainable from acrylate esters with α-phosphate ester groups.

Fig. 6 shows thermogravimetric curves measured for the copolymers. They indicate that incorporation of DMEVP units in the copolymers reduces their thermal stability.

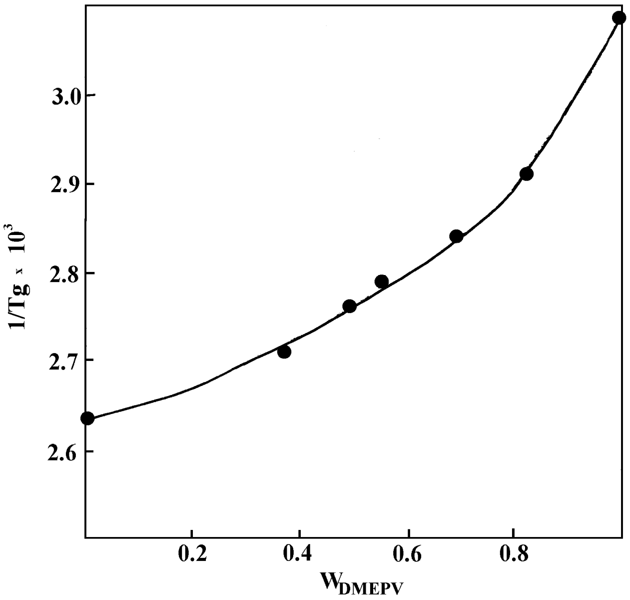

Fig. 5. Measured and calculated $1/T_g$ values versus the weight fraction of styrene in the copolymers. The calculated line is based on Eq. 2, where $T_{g,polystyrene}$, $T_{g,polyDMEVP}$ and $T_{g,Alt}$ are 378, 323 and 358 K, respectively.

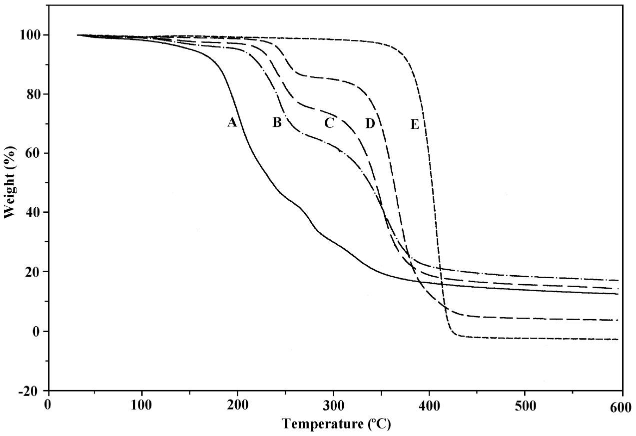

Fig. 6. TGA curves for polyDMEVP (A) and DMEVP–styrene copolymers containing 49.3 (B), 62.8 (C), 79 (D) and 100 (E) mol% styrene.

PolyDMEVP begins to decompose at about 150 °C and approximately one-half of the sample is lost below 200 °C. Similarly, an initial weight loss amounting to approximately one-half the mass of the DMEVP units present took place below 270 °C when the copolymers were heated. Loss of dimethyl phosphate from DMEVP units is a possible explanation for this. A substantial amount of char, up to 25 wt%, remained after polyDMEVP and the copolymer samples were heated to 400 °C and the amount of it did not change from 400 to 600 °C. This tendency to form char may have a valuable influence on the flame resistance of polymers containing DMEVP units.

4. Conclusions

DMEVP, a representative member of the class of acrylate monomers with α-phosphate ester substituents was easily synthesized by the Perkow reaction and found to polymerize easily. Copolymers of this monomer with styrene were prepared, characterized and evaluated for thermal properties. Reactivity ratios determined for the styrene–DMEVP system indicated a strong tendency of the monomers to cross-propagate. Based on its ease of copolymerization and the tendency of DMEVP-containing polymers to form char on pyrolysis, it seems that DMEVP and related monomers have potential value for the synthesis of polymers with good combustion resistance. Additional studies in this area are highly recommended.

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