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I. Sideridou-karayannidou[a]; G. Karayannidis[a]; P. Mavros[a]; K. A. Tsoleridis[a]; M. Tzitzidou[a]
[a] Department of Chemistry, Aristotle University, Thessaloniki, Greece

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COPOLYMERIZATION OF *N*-VINYLCARBAZOLE WITH 2-DIMETHYLAMINOETHYL METHACRYLATE

I. SIDERIDOU-KARAYANNIDOU,* G. KARAYANNIDIS, P. MAVROS,
K. A. TSOLERIDIS, and M. TZITZIDOU

Department of Chemistry
Aristotle University
GR-540 06 Thessaloniki, Greece

ABSTRACT

The thermal copolymerization of *N*-vinylcarbazole (VCz) with 2-dimethylaminoethyl methacrylate (DMAEM) initiated by α,α'-azobisisobutyronitrile (AIBN) in solution in tetrahydrofuran at 60°C has been studied. Different compositions of copolymer were prepared and characterized by UV, IR, and ^{1}H-NMR spectroscopy, viscosity measurements, and thermal studies. The estimation of the composition of VCz and DMAEM in the copolymer was carried out by UV spectroscopy. The reactivity ratio of VCz (r_1) and DMAEM (r_2) was determined by the methods of Mayo and Lewis, Kelen and Tüdös, and Tidwell and Mortimer.

INTRODUCTION

Poly(*N*-vinylcarbazole)† (PVCz) is a polymer of considerable current interest because of its unusual electrical and photoelectrical properties. It has been used as a photoconductor in electrophotography [1–3].

However, it is a stiff, brittle material with high glass transition temperature (Tg = 227°C) [4]. Copolymerization of VCz with suitable monomers could soften the resulting product, leading to better film properties. Thus, copolymers of VCz with *n*-butyl acrylate, dibutyl maleate, or vinyl 2-ethylhexanoate showed Tg values considerably lower than that of homopolymer and produced softer and more pliable

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†Systematic IUPAC name: poly[1-(*N*-carbazolyl)ethylene].

films [5]. Also, copolymers of VCz with a series of alkyl methacrylates with varying length of the side group showed a regular decrease of Tg, revealing that the methacrylic constituent unit acts as an internal plasticizer [6].

In this paper, the results of thermal copolymerization of VCz with 2-dimethylaminoethyl methacrylate (DMAEM) are reported. The use of DMAEM as a comonomer is of interest because the DMAEM homopolymer (PDMAEM)* has low glass transition temperature (Tg = 19°C) [7] and is water-soluble with good film-forming properties [8]. The development of water-soluble or dispersable photoconductive materials is of particular importance, because of the pollution problems presented in coating and casting by the use of organic solvents. Water-soluble or dispersable copolymers containing VCz were first synthesized by Mulvaney and Chang [9].

EXPERIMENTAL

Materials

N-vinylcarbazole (VCz) (from Aldrich) and *N*,*N*-dimethylaminoethyl methacrylate (DMAEM) (from Merck) were used as received. α,α'-Azobisisobutyronitrile (AIBN) (from Fluka) was recrystallized from methanol. Tetrahydrofuran (THF) was used as the polymerization solvent (purum, from Merck).

Copolymerizations

All polymerizations were carried out in glass tubes with an i.d. of 1.0 cm. A typical polymerization solution comprised 0.85 g of monomers (in the appropriate molar ratio), 0.0041 g (o.5 mol%) of AIBN, and 5 mL of THF. The colorless polymerization solution was degassed by bubbling nitrogen for about 10 min. Then the tube was stoppered and placed in a water bath thermostated at 60°C. Nine copolymerizations were performed at various initial monomer feed ratios (Table 1). All polymerizations proceeded in homogeneous phase and were interrupted at low conversions of the monomers to copolymers. The copolymer solution was poured into petroleum ether (b.p. 40-60°C) and a white copolymer was obtained, which was isolated by discarding the supernatant clear solution; only in the case where the initial monomer feed ratio was 0.9:0.1 (VCz:DMAEM) was the resulting copolymer isolated by filtration. Copolymers were purified by dissolving in THF and precipitating in petroleum ether and dried at 60°C under vacuum to constant weight.

Homopolymerizations

Homopolymers of VCz and DMAEM were also prepared under the same experimental conditions used for copolymers. PVCz was isolated from the polymerization solution by pouring it in methanol and filtrating, in contrast to the PDMAEM, which after precipitation in petroleum ether was isolated by discarding the supernatant clear solution. Both homopolymers were purified by dissolution in THF and precipitation in petroleum ether.

*Systematic name: poly[1-(2-dimethylaminoethoxycarbonyl)-1-methylethylene].

Characterization of the Polymers

The copolymer composition was determined from UV spectra. These were taken with a Pye-Unicam SP-8000 spectrophotometer. IR spectra of copolymers were recorded on a Perkin Elmer 297 spectrophotometer on KBr pellets. ^{1}H-NMR spectra of copolymers were recorded at ca. 40°C on a Bruker 80-MHz instrument with $CDCl_3$ as the solvent and TMS as the internal reference. The inherent viscosity (η_{inh}) measurements were performed in an Ubbelohde viscometer at 25°C with $CHCl_3$ as solvent (c = 0.5%). The glass transition temperature (Tg) was determined with a Perkin Elmer Differential Scanning Calorimeter (DSC-2) at a heating rate of 20°C/min and scan range 2 mcal/sec. The Thermogravimetric Analysis (TGA) was carried out using a Perkin Elmer thermobalance (TG-2) in nitrogen atmosphere at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

VCz and DMAEM were polymerized at 60°C in THF solution, using AIBN as initiator. Identification of the reaction product was of primary importance, because it is known that VCz in the presence of electron acceptors can form charge transfer complexes that can lead to the cationic homopolymerization of VCz and also that VCz is easily homopolymerized cationically by acidic impurities present in the reaction system [10]. Thus, it has been reported that the polymerization of VCz with methyl methacrylate by AIBN gave a mixture of a copolymer and VCz homopolymer (PVCz) [11]. However, a later study of this polymerization showed that it gives only the copolymer [12, 13]. Also, study of the polymerization of the VCz with *n*-butyl acrylate by AIBN in THF solution indicated that spontaneous homopolymerization of VCz as well as copolymerization with *n*-butyl acrylate occurs, unless VCz and THF are rigorously purified [5].

The studied polymerization of VCz and DMAEM by AIBN under the reported conditions gave only the copolymer of the two monomers. Its structure was confirmed by ^{1}H-NMR spectroscopy. The 80-MHz spectra of PVCz (Fig. 1a) showed two extremely high field signals in the aromic region (4.9 and 6.4 δ) due to the shielding effect of neighboring carbazyl groups [14]. These high field peaks were not observed in the ^{1}H-NMR spectrum of the reaction product of VCz and DMAEM, obtained from different monomer feed ratios (Fig. 1b,c). This is a clear indication that there are no long runs of VCz-mers in the reaction products and that it is a copolymer. A part of the copolymerization solution was also poured into methanol and no precipitate appeared, indicating that there is no PVCz, since PVCz is insoluble in methanol. At the same time, the UV spectrum of a solution of VCz and DMAEM in THF did not show the existence of a charge transfer complex between the two monomers even after heating. Moreover, when this solution was heated in the absence of AIBN, no polymerization took place.

The copolymers prepared were also characterized by IR analysis (Fig. 2). The IR spectrum of the copolymer showed the characteristic absorption band of ester group at 1720 cm^{-1} and of carbazyl group at 1620 and 1590 cm^{-1}.

The copolymer compositions (Table 1) were determined by UV spectroscopy. The determination was based on the absorption band of the carbazyl moiety of

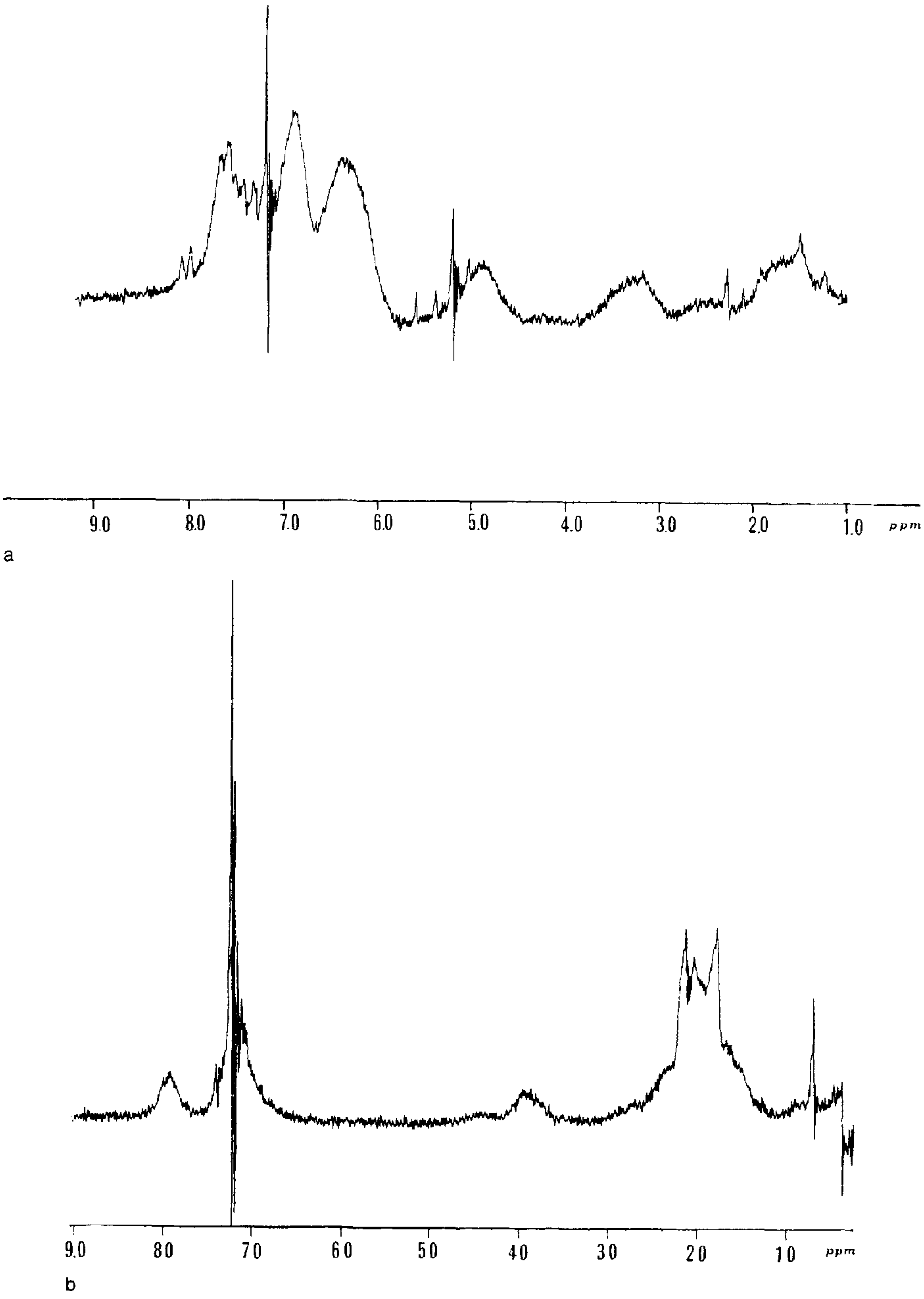
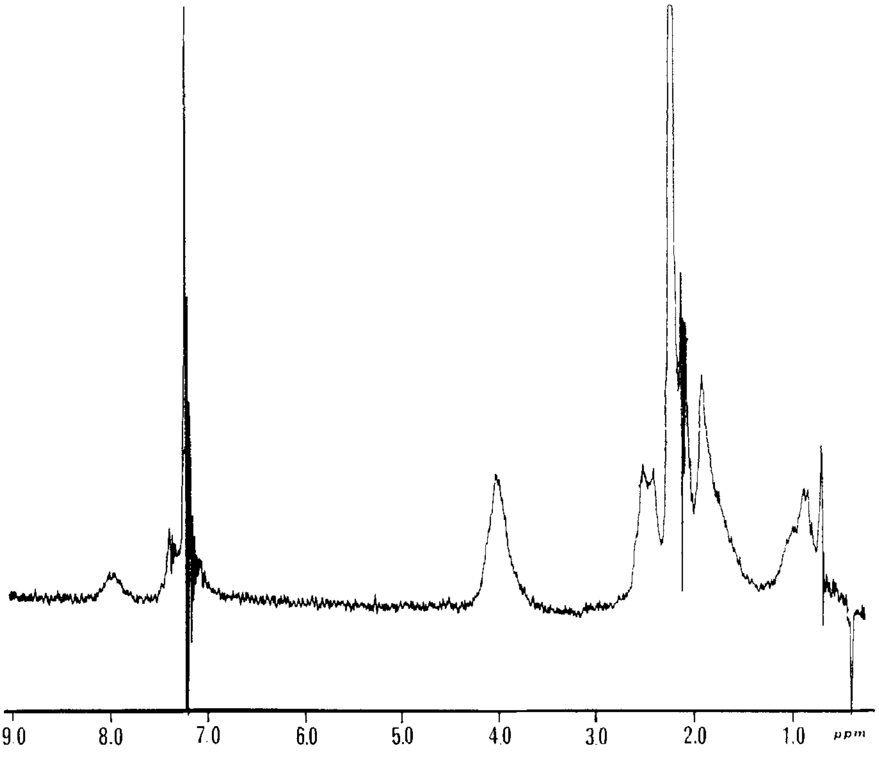


FIG. 1. 80-MHz ^{1}H-NMR spectrum in chloroform-d of VCz homopolymer (a), of VCz-DMAEM copolymer obtained by monomer feed ratios (VCz:DMAEM) of 70:30 (b) and 30:70 (c).



c

FIG. 1. Continued.

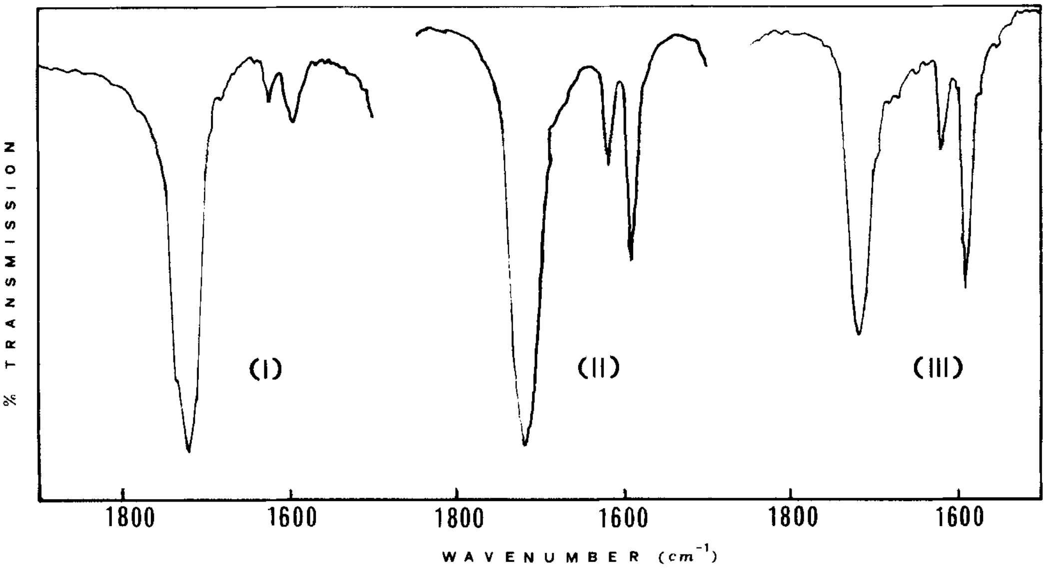


FIG. 2. IR spectra of copolymers VCz-DMAEM obtained by different monomer feed ratios (VCz:DMAEM) : (I) 20:80; (II) 50:50; (III) 80:20.

TABLE 1. Copolymer Compositions and Yields of VCz-DMAEM Copolymers

M_1 VCz in monomer feed (mol%)	Conc. of copolymer (mg/ 100 mL)	Absorb. at 343 nm	Conc. of VCz in copolymer (mg/100 mL)	VCz in copolymer (wt%)	Mmol VCz in 100 g copolymer	Mmol DMAEM in 100 g copolymer	m_1 Conc. of VCz in copolymer (mol%)	Yield (wt%)
10	20.0	0.21	1.55	7.7	40.1	586.8	6.4	10.7
20	32.2	0.69	5.09	15.8	81.8	535.5	13.3	10.6
30	31.8	0.83	6.13	19.3	99.7	513.5	16.3	11.0
40	17.5	0.69	5.09	29.1	150.6	451.0	25.0	10.3
50	8.9	0.44	3.25	36.5	188.8	404.0	31.9	9.8
60	7.3	0.44	3.25	44.5	230.2	353.1	39.5	10.9
70	6.8	0.47	3.47	51.0	264.0	311.6	45.9	9.9
80	6.0	0.47	3.47	57.8	299.2	268.3	52.7	9.0
90	4.9	0.46	3.39	69.3	358.5	195.4	64.7	9.2

According to the calibration curve used, the absorbance of PVCz (5.86 mg/100 mL of THF) at 344 nm is 0.794.

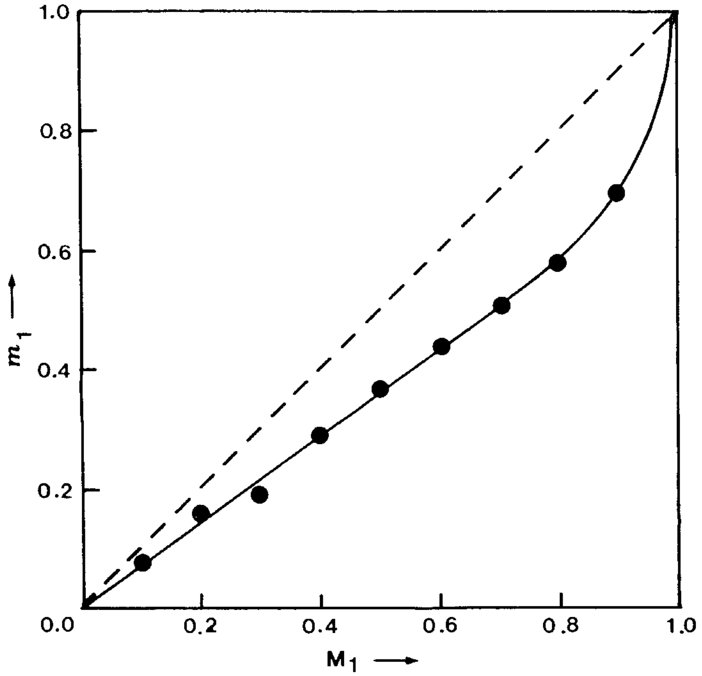


FIG. 3. Relationship of the molar fraction VCz in the monomer feed (M_1) and the molar fraction in the copolymer (m_1) in VCz-DMAEM copolymerization.

copolymers observed at 343 nm. For calculation of the molar fraction of VCz in each copolymer, it was assumed [15] that the molar extinction coefficient value of the carbazyl group does not change between PVCz and the copolymer and their absorption maxima. PVCz prepared under the same experimental conditions as the copolymers showed the carbazyl group absorption maximum at 344 nm.

Absorption values at 344 nm obtained from UV spectra of PVCz solutions with different concentrations were plotted against the concentration. Then the absorbance values of the VCz component of copolymers were found and the wt% values of VCz in the copolymers were calculated. These were converted to mol%

TABLE 2. Calculation of the Reactivity Ratios by Various Methods

Method	r_1	r_2	$\Sigma\{m_1{}^a(\text{exp}) - m_1(\text{calc})\}^2$	Ref.
Mayo and Lewis	0.13	1.53	0.0017	16
Kelen and Tüdös	0.15	1.55	0.0017	17
Tidwell and Mortimer	0.14	1.48	0.0015	18

[a] m_1 = VCz content of the copolymer [mol%].

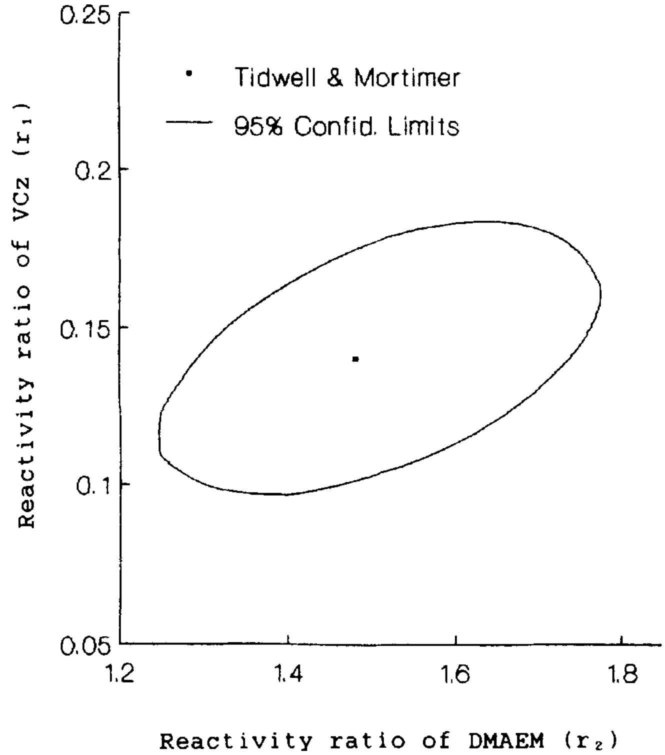


FIG. 4. Estimated 95% joint confidence limits of r_1 and r_2 calculated by the Tidwell-Mortimer method, for the copolymerization of VCz (r_1) and DMAEM (r_2).

using the molecular weights of the monomers. The dependence of the molar fraction of the VCz in the copolymer on the molar fraction of the VCz in the monomer feed is shown in Fig. 3.

The reactivity ratios of VCz (r_1) and DMAEM (r_2) were calculated according to the methods of Mayo and Lewis [16], Kelen and Tüdös [17], and Tidwell and Mortimer [18]. The results are shown in Table 2, together with the sum of squares of the deviations of the calculated from the experimental copolymer compositions; it is obvious that the reactivity ratios calculated with the Tidwell and Mortimer method ($r_1 = 0.14$ and $r_2 = 1.48$) give the closest fit to the experimental data.

The estimated 95% joint confidence limits of r_1 and r_2, as calculated by the Tidwell and Mortimer method, were also plotted, as shown in Fig. 4. The reactivity ratios of VCz ($r_1 < 1$) and DMAEM ($r_2 > 1$) indicate that in this copolymerization the incorporation of DMAEM in the copolymer is favored.

The copolymers prepared were soluble in THF and $CHCl_3$ but insoluble in water, even at the highest content of DMAEM. They showed good film-forming properties. The higher the DMAEM content in the copolymer, the more soft and pliable is the film obtained. The results of the inherent viscosities of copolymers are summarized in Table 3. They showed a maximum value for the copolymer with about equal content (wt%) of the two monomers.

The glass transition temperature (Tg) of the copolymers was determined by a

TABLE 3. Viscosities and Thermal Properties of Homopolymers and Copolymers

				First stage		Second stage		Third stage	
VCz in feed (mol%)	Weight fraction of VCz in copolymer (wt%)	η_{inh} (dL/g)	Tg (°C)	Tm[a] (°C)	Weight loss (%)	Tm (°C)	Weight loss (%)	Tm (°C)	Weight loss (%)
0	0.0	–	18	350	47	457	45	–	–
10	7.7	–	27	352	46	463	46	–	–
20	15.8	–	37	347	45	465	51	–	–
30	19.2	.48	39	350	42	470	54	–	–
40	29.1	–	55	536	48	477	47	–	–
50	36.5	.55	64	348	46	465	47	–	–
60	44.5	.56	73	347	33	455	56	–	–
70	51.0	.51	82	335	25	455	68	–	–
80	57.8	–	84	346	35	387	32	445	17
90	69.3	.34	108	345	28	408	47	446	15
100	100.0	.10	212	490	100	–	–	–	–

[a] Temperature of weight loss with maximum rate.

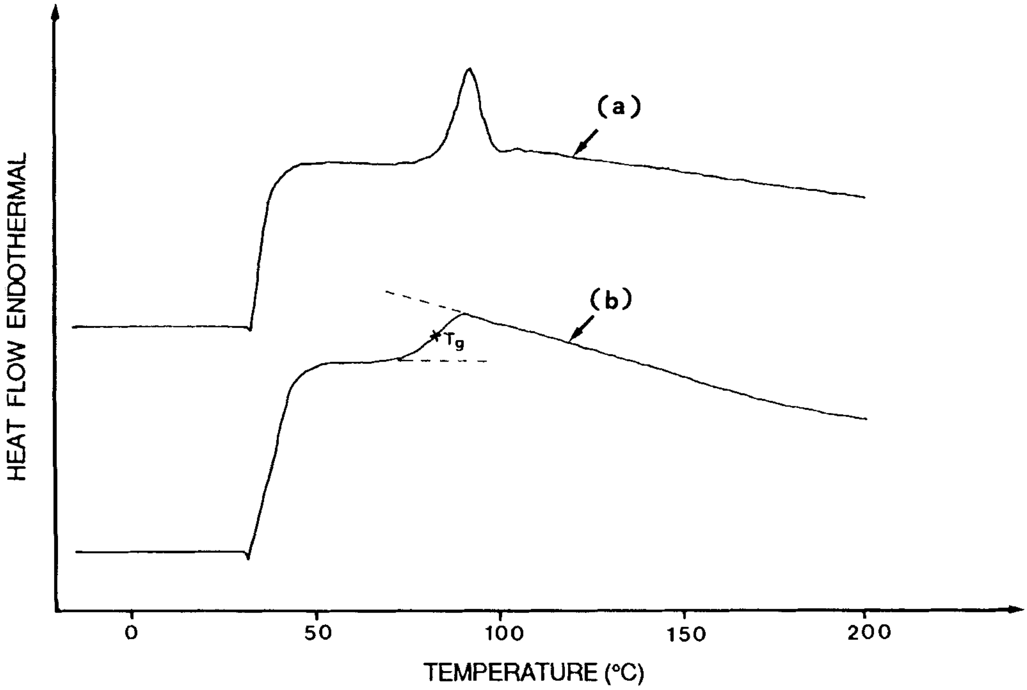


FIG. 5. DSC curves at the glass transition of a copolymer VCz-DMAEM. (a) First run; (b) after quenching.

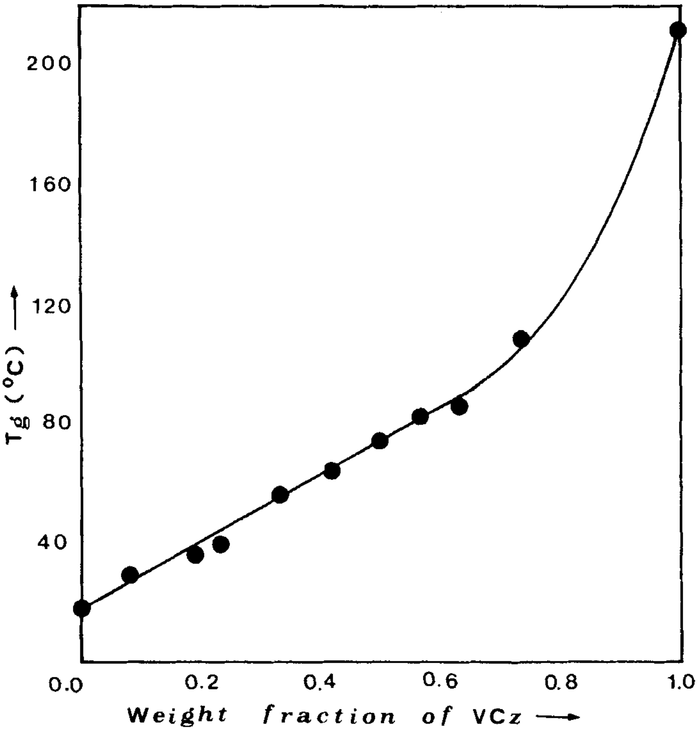


FIG. 6. Relationship between Tg (°C) and weight fraction of VCz in copolymer VCz-DMAEM.

TABLE 4. Temperature of Decomposition at Different Weight Losses of VCz and DMAEM Homopolymers and Copolymers

Vcz in feed (mol%)	VCz in copolymer (wt%)	Weight loss of:			
		20%	40%	60%	80%
0	0.0	330	346	428	452
10	7.7	335	352	436	460
20	15.8	333	350	436	455
30	19.2	335	362	445	463
40	29.1	345	415	458	470
50	36.5	334	405	440	460
60	44.5	335	400	430	460
70	51.0	331	388	421	450
80	57.8	328	368	403	455
90	69.3	345	380	408	445
100	100.0	450	468	479	490

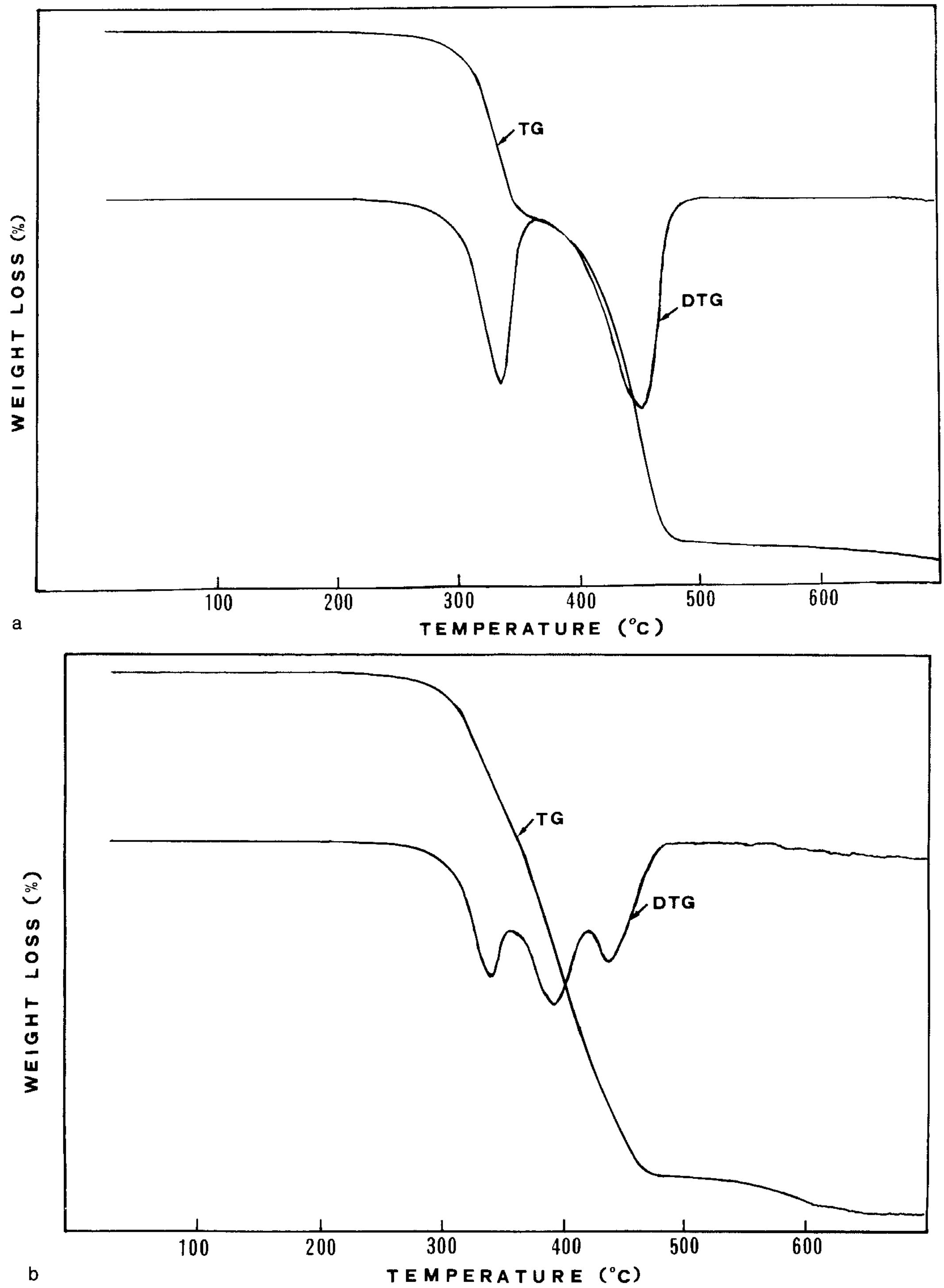


FIG. 7. TG and DTG curves of copolymer obtained from monomer feed (a) 50:50 and (b) 90:10.

differential scanning calorimeter (DSC). During the first dynamic DSC experiment, an endothermic peak was observed in the transition region (Fig. 5a). This peak must be due to the enthalpy relaxation, which superimposes the Tg, because it was not observed in the second DSC run, after quenching of the sample (Fig. 5b). The Tg values of the copolymers, as shown in Table 3, are considerably lower than that of the PVCz (212°C) prepared under the same experimental conditions as the copolymers. The decrease of Tg with the increase of weight fraction of DMAEM in the copolymer (Fig. 6) is approximately linear, but it is curved near the end-point of PVCz, due probably to free volume effects.

The results of thermogravimetric (TG) and derivative thermogravimetric analysis (DTG) of copolymers and homopolymers are summarized in Tables 3 and 4. The decomposition of PDMAEM took place in two well-separated stages with maximum rate at 350°C (47% weight loss) and 457°C (45% weight loss), in contrast to PVCz, which decomposed in one stage with maximum rate at 490°C.

The degradation of PDMAEM seems to proceed like that of other poly-*n*-alkyl methacrylates through two competing reactions, viz. depolymerization to monomer and ester decomposition resulting in poly(methacrylic acid) and the corresponding olefin formation [19, 20]. As far as the thermal degradation of PVCz is concerned, experimental results showed that it breaks up almost completely into the monomer through a stepwise unzipping mechanism [21]. All the copolymers of VCz and DMAEM showed two steps of decomposition (Fig. 7a) with a maximum rate of 335–356°C and 445–477°C (Table 4). Copolymers with high content of VCz (57.8 and 69.3 wt%) also showed a third step of decomposition between the two abovementioned steps (Fig. 7b) with maximum rate at 387–407°C. Generally, the thermal stability of copolymers was lower than that of PVCz and slightly higher than that of PDMAEM.

CONCLUSIONS

Copolymerization of VCz and DMAEM by AIBN in THF at 60°C gave only the copolymer of the monomers. The reactivity of DMAEM ($r_1 > 1$) was found to be higher than that of VCz ($r_2 < 1$). The copolymers prepared from varying monomer feed ratios showed Tg values considerably lower than that of PVCz; they also showed good film-forming properties, especially those with high DMAEM content.

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