

Copolymers of *N*-Vinylcarbazole and *N,N*-Dimethylaminoethyl Methacrylate

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ABSTRACT: Copolymers of *N*-vinylcarbazole (NVC) and *N,N*-dimethylaminoethyl methacrylate (DMAEMA) were prepared by free-radical polymerization in a toluene solution at 60°C using 2,2'-azobisisobutyronitrile (AIBN) as an initiator. The reactivity ratios of both monomers were calculated using the extended Kelen–Tüdös method and found to be $r_1 = 0.441 \pm 0.052$ and $r_2 = 1.632 \pm 0.102$. The microstructure of copolymer chains is described on the basis of first-order Markov statistics. The microstructure of copolymers was also studied by UV and ¹H-NMR spectroscopy. Copolymers were characterized by viscosity and number-average molecular weight (\bar{M}_n) measurements. The glass transition temperatures (T_g) of the copolymers were determined calorimetrically and the variation of T_g with the copolymer composition is discussed. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1815–1824, 1997

INTRODUCTION

Poly(*N*-vinylcarbazole) (PNVC) is a specialty material of considerable academic and industrial interest, because of its unusual electric and photoelectric properties.^{1,2} It has been used as a high-temperature dielectric material in the electric industry³ and as a photoconductor in photocopies and electrophotographic printing plates.^{4–6} However, due to the bulkiness of the carbazole groups, the chains are stiff in nature and the polymer has a glass transition temperature of 227°C,⁷ which is among the highest known for vinyl polymers. Also, the usual solvents for PNVC are tetrahydrofuran and toluene, which are not suitable for use in the reprographics industry. Copolymerization of NVC with alkyl(methacrylates) was found to soften the resulting product, leading to better film properties, because these monomers act as internal plasticizers.^{8,9} Guthrie et al., in a recent publication, studied the copolymerization of NVC with acrylic and methacrylic acid in an effort to prepare alkali-soluble copolymers of NVC suitable for use

as a part of a photoconductive lithographic printing plate assembly.¹⁰

In our previous work, we prepared the copolymers of NVC and 2-dimethylaminoethyl methacrylate (DMAEMA) by photoinduced charge-transfer copolymerization¹¹ and thermal copolymerization induced by AIBN.¹² The use of DMAEMA as a comonomer is of interest because the DMAEMA homopolymer has a low glass transition temperature ($T_g = 19^\circ\text{C}$)¹³ and is soluble in water as well as in many organic solvents with good film-forming properties.¹⁴ The thermal copolymerization of NVC and DMAEMA was carried out in a solution in tetrahydrofuran and found to follow the simple terminal model of copolymerization; the reactivity ratios of the monomers were roughly evaluated. This work is concerned with the copolymerization of the same monomers but in a nonpolar solvent, such as toluene, the precise determination of the reactivity ratios, and the study of the microstructure and some physical properties of copolymers.

EXPERIMENTAL

Reagents

N-Vinylcarbazole (NVC) was supplied by Aldrich (98%, mp 64–66°C) and recrystallized from meth-

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Table I Experimental Data of NVC–DMAEMA Copolymers Prepared in Toluene Solution at 60°C in the Presence of AIBN

Molar Fraction of NVC in Feed (M_1)	Conversion ^a (Wt %)	Molar Fraction of NVC in Copolymer ^a (m_1)	Mean Sequence Length ^b	
			\bar{l}_1	\bar{l}_2
0.10	12.3	0.065	1.05	15.69
0.20	5.8	0.129	1.11	7.53
0.30	16.9	0.212	1.19	4.81
0.40	4.5	0.262	1.29	3.45
0.50	7.9	0.348	1.44	2.63
0.60	8.1	0.426	1.66	2.09
0.70	14.4	0.556	2.03	1.70
0.80	14.1	0.677	2.76	1.41
0.90	10.8	0.811	4.98	1.18

^a Average experimental values from three series of copolymerization experiments.

^b $\bar{l}_1 = r_1([M_1]/[M_2]) + 1$ and $\bar{l}_2 = r_2([M_2]/[M_1]) + 1$; $M_1 = \text{NVC}$, $M_2 = \text{DMAEMA}$.

anol (mp 65–66°C). *N,N*-Dimethylaminoethyl methacrylate was supplied by Merck (>98%), distilled at 83–84°C/18 mmHg before use, and stored at 0°C. α,α' -Azobisisobutyronitrile (AIBN) provided by Fluka (>98%, mp 102–104°C) was recrystallized from methanol (mp 103–104°C). Toluene, used as polymerization solvent, was analytical grade from Riedel-de Haen (99%) and used as received.

Copolymerization Procedure

All copolymerizations were carried out in glass tubes which were shaken in a 60°C water bath for a certain time. The starting overall concentration of the two comonomers was 1.00 mol/L, and that of the initiator (AIBN), 0.05 mol/L. The reaction solution was flushed with nitrogen for 2 min prior to copolymerization. Nine copolymerizations were performed at various initial comonomer ratios expressed through the molar fraction (M_1) of the first comonomer (Table I). For each initial comonomer ratio, three copolymerizations were made. Copolymerizations at all monomer ratios proceeded in a homogeneous phase. Copolymers were isolated by precipitation in cold petroleum ether (bp 40–60°C) and purified by two precipitation-dissolving cycles in tetrahydrofuran and petroleum ether. These were exhaustively dried under a vacuum at 60°C to constant weight for the gravimetric determination of the weight-conversion percentage of the corresponding polymerization experiment. The average weight monomer conversion and copolymer composition for each monomer ratio is shown in Table I.

Copolymer Characterization

Copolymer compositions were determined by UV spectroscopy using a Hitachi U-2000 spectrophotometer. The determination was based on the characteristic absorption band of the carbazole chromophore of copolymers observed at 342.5 nm in dioxane solutions, assuming that the molar extinction coefficient is independent of the carbazole content of the copolymer. The validity of this method was confirmed first by Tada et al.¹⁵ and then by Chiellini,^{16,17} by the excellent correlation of the results obtained by UV spectroscopy with those taken by elemental analysis and NMR spectroscopy. The copolymer compositions were calculated from the extinction coefficient value of the carbazolyl group in the NVC homopolymer prepared under the same experimental conditions as were the copolymers. Absorption values at 343 nm obtained from UV spectra of the NVC homopolymer solutions in dioxane with different concentrations were plotted against the concentration to give a value for $\epsilon = (2.861 \pm 0.189) \cdot 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$.

UV spectra of copolymers were also taken in dichloromethane solutions in the region of 220–250 nm. ¹H-NMR spectra of copolymers and of poly(*N*-vinylcarbazole) were recorded on a Bruker 300 MHz instrument with CDCl₃ as the solvent and TMS as the internal reference. Viscosity measurements (η_{inh}) were performed by an Ubbelohde viscometer at 25°C in tetrahydrofuran ($c = 0.5\%$). Number-average molecular weight (\bar{M}_n) measurements were performed by a “Knauer” membrane osmometer in THF solution

at 37°C. The glass transition temperature (T_g) was determined with a Perkin-Elmer differential scanning calorimeter (DSC-2) at a heating rate of 20°C/min and scan range 2 mcal/s.

Determination of Monomer Reactivity Ratios

The monomer reactivity ratios r_1 and r_2 were experimentally determined using the extended Kelen-Tüdös method, which takes into account the weight conversion of comonomers.¹⁸ The 95% confidence limits of these ratios were calculated by the method proposed also by Kelen-Tüdös.¹⁹ The reactivity ratios were also calculated by the Alfrey-Price equation based on the Q and e values of the monomers.

RESULTS AND DISCUSSION

The copolymerization of NVC with DMAEMA at 60°C in the presence of AIBN in toluene solutions was studied in a wide composition interval with a molar fraction of NVC ranging from 0.10 to 0.90 in the monomer feed. The results of these polymerization experiments are shown in Table I.

From the data of Table I, the reactivity ratios of NVC and DMAEMA were determined by application of the Kelen-Tüdös high-conversion formula,¹⁸ which is based on the terminal model of copolymerization. In our previous work,¹² we found that NVC addition does follow the terminal model in copolymerization with DMAEMA, as it also occurs with other alkyl methacrylates.^{17,20,21} The determined reactivity ratios and the 95% confidence limits were

$$r_1(\text{NVC}) = 0.441 \pm 0.052;$$

$$r_2(\text{DMAEMA}) = 1.632 \pm 0.102$$

These values show that both radicals prefer DMAEMA and that copolymers are enriched in DMAEMA units. The product $r_1 r_2 (= 0.72)$, which is a criterion of the tendency of monomers toward alternation or randomness, shows that these monomers have the tendency to give random copolymers. Taking into account the Lewis-Mayo classical copolymerization equation and the values of r_1 and r_2 , the composition diagram shown

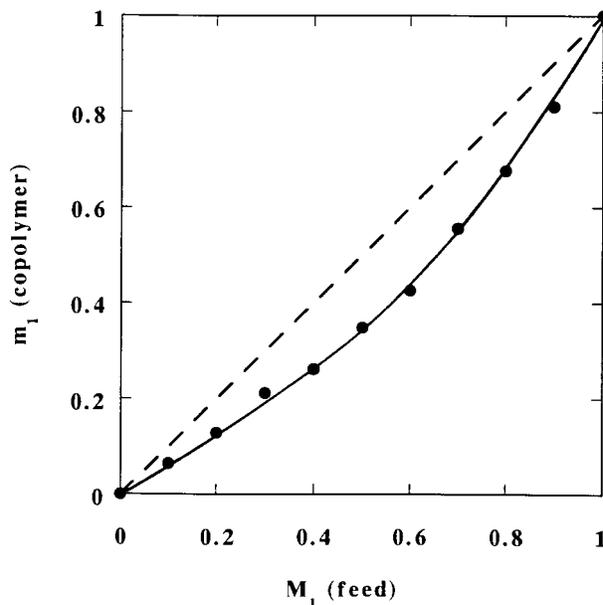


Figure 1 Composition diagram for NVC/DMAEMA copolymerization: M_1 , molar fraction of NVC in the feed; m_1 , mol fraction of NVC in the copolymer. The solid line corresponds to the theoretical composition diagram deduced from the reactivity ratios ($r_1 = 0.44$, $r_2 = 1.63$).

in Figure 1 was drawn. The experimental composition data fit adequately the theoretical composition represented in the Figure 1 by the solid line.

Comparison of the r_1 and r_2 values determined in this work in toluene with those obtained in tetrahydrofuran (THF) in our previous work¹² ($r_1 = 0.14$, $r_2 = 1.48$) shows that the copolymerization solvent influences the relative reactivity of the monomers. THF is a more polar solvent ($\epsilon = 7.6$) than is toluene ($\epsilon = 2.4$) and most probably increases the polarity of NVC and DMAEMA. These monomers have opposite polarities and an increase of their polarities can lead to an increase of the tendency of NVC and DMAEMA for alternation in the polar THF.

Reactivity ratios of NVC and DMAEMA could be calculated by using the Alfrey-Price equations and the Q and e values of the monomers, which are reported in the literature and are shown in Table II. It is noteworthy that while the Q and e values of NVC are based on the copolymerization of NVC with 12 other monomers the values of DMAEMA are based only on the copolymerization of DMAEMA with styrene. However, these values are close enough to those calculated from the ¹³C-NMR absorption frequencies of the α - and β -carbon atoms of DMAEMA. Taking into account the Q and e values of NVC and those of DMAEMA ($Q_2 = 0.66$ and $e_2 = 0.49$) determined under poly-

Table II Q and e Values of NVC and DMAEMA Found in the Literature

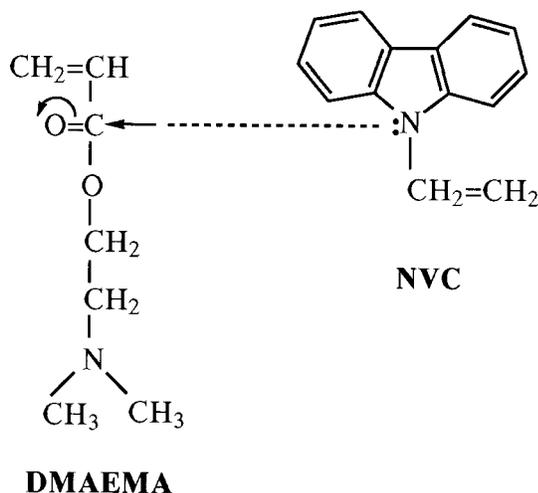
Monomer	Q	e	Comonomer	Copolymerization Conditions	Ref.
NVC	0.26	-1.29	^a	—	22
DMAEMA	0.59 ^b	0.38 ^b	—	—	23
DMAEMA	0.68	0.48	Styrene	Bulk, 60°C	24
DMAEMA	0.66	0.49	Styrene	Benz. 50°C	25
DMAEMA	0.74	0.81	Styrene	DMF, 50°C	25

^a Twelve different monomers were used and the Q and e values were determined by the linear least-squares evaluation of the corresponding reactivity ratios.

^b These values were calculated from the ^{13}C -NMR absorption frequencies of the a- and b-carbon atoms of DMAEMA.

merization conditions closer to our experiments, the reactivity ratios of both monomers were calculated to be $r_1 = 0.040$ and $r_2 = 1.061$.

These theoretical values of r_1 and r_2 show a higher tendency of NVC and DMAEMA for alternation in copolymerization than do those experimentally determined. The theoretical product $r_1 r_2 (=0.042)$ is much lower than is the experimental $r_1 r_2 (=0.72)$. This discrepancy of the values might suggest the existence of polar interactions between the two comonomers which change the Q and e parameters. NVC is a typical electron-donating monomer ($e = -1.29$) that undergoes charge-transfer polymerization, i.e., polymerization by electron acceptors.²⁶ On the other hand, DMAEMA is an electron acceptor monomer characterized by a positive polarity of its vinyl bond. This difference in the electron behavior of the two comonomer molecules could lead to donor-acceptor interactions between their molecules like this:



Such an interaction would cause a decrease in the polarity of NVC and an increase in the polarity of DMAEMA. Study of the UV spectra of NVC and DMAEMA solutions did not show the exist-

tence of a charge-transfer complex even after heating.¹² But the registration of a charge-transfer complex is difficult when the value of the equilibrium constant of the complex formation is small. So, the existence, during copolymerization, of a weak charge-transfer complex or at least charge-transfer interactions not leading to the formation of a true molecular complex could not be excluded. Nevertheless, it was found²⁷ that *N*-vinylpyrrolidone (NVP), an electron-donor monomer analogous to NVC with polarity $e = -1.62$,²² forms with methyl methacrylate (MMA) ($e = 0.40$),²² which is analogous to DMAEMA, a true charge-transfer complex, which causes an increase of the polarity of MMA and mainly a decrease of the polarity of NVP.

The microstructure of the prepared copolymers was examined on the basis of first-order Markov statistics. Taking into account well-known statistical relations and the determined values of reactivity ratios $r_1 (=0.441)$ and $r_2 (=1.632)$ the "run number" (R) of the copolymers was calculated. This parameter is defined²⁸ as the average number of monomer alternations in a copolymer per 100 monomeric units and provides a useful picture of the sequence distribution in a copolymer chain. The variation of R with the NVC molar fraction in the monomer feed is shown in Figure 2. It is observed that the maximum value of $R = 54$ is reached for an NVC molar fraction in the monomer feed of about 0.60–0.70.

The distribution of monomeric units of the prepared copolymers in terms of the mean sequence length as calculated on the basis of the determined values of reactivity ratios is presented in Table I. The results show the rapid buildup of NVC in the copolymer when moving from lower to higher NVC feeds and leading to $\bar{l}_1 > \bar{l}_2$. The difference between \bar{l}_1 and \bar{l}_2 values is reduced considerably in the range of the molar fraction of NVC in the monomer feed of 0.6–0.7, where about

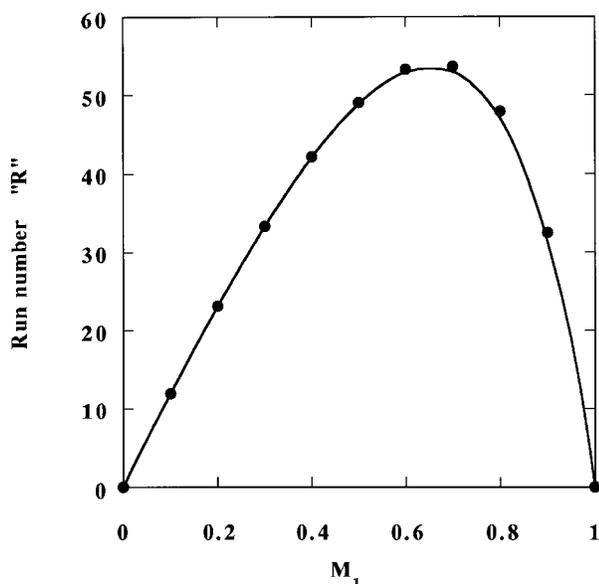


Figure 2 Variation of the "run number" (R) of copolymer with the monomer feed composition; M_1 , molar fraction of NVC.

an equimolecular amount of both monomers is incorporated into the copolymer. The distribution of monomeric units in that copolymer may be expressed as -1122-

The distribution of monomeric units of the prepared copolymers can be also expressed in terms of distribution of sequence lengths (Table III). These data show that increasing the molar fraction of NVC in the copolymer causes the distribution of sequence length to flatten and broaden. It is worthy to note that in the copolymer obtained

from a monomer feed of 70/30 and with an NVC content of 55.6 mol % and mean sequence length $\bar{l}_1 = 2.03$ (-1122-) only 25% of NVC units are in a sequence of length $n = 2$, while 49.3% is sandwiched between two DMAEMA units and the rest (25.7%) belongs to longer sequences $n \geq 3$.

The microstructure of the prepared copolymers was also studied by UV spectroscopy. The UV spectra of copolymer solutions in CH_2Cl_2 show in the region of 220–250 nm two bands at 230 and 238 nm (Fig. 3). As the content of NVC in the copolymers is increased, the relative intensity of the above two peaks changes and the peak at 230 nm becomes predominant.

Comparison of the UV spectra of copolymers with that of poly(*N*-vinylcarbazole) (PNVC) and of *N*-isopropylcarbazole (NIPC), which is a low molecular weight model compound, can give useful information about the microstructure of copolymers. The UV spectrum of PNVC shows at about the same region a peak at 230 nm and a shoulder at about 238 nm. On the contrary, in NIPC, the absorption at 238 nm is prominent while the 230 nm absorption is present as a slight shoulder.²⁹ So, it has been suggested^{17,29} that the absorption at 230 nm is due to electronically interacting nearest-neighbor carbazole units, whereas that at 238 nm is characteristic of the isolated carbazole unit. In Table III is presented the % molar fraction of isolated ($n = 1$) and interacted carbazole chromophores ($n \geq 2$) calculated from the determined reactivity ratios. From these data and taking into account the value of the ratio $A_{230} : A_{238}$ in NIPC and PNVC, the theoretical value of the above ratio

Table III Relationship Between Chemical Composition, Distribution of Sequence Lengths, and UV Spectral Data of NVC–DMAEMA Copolymers

Molar Fraction of NVC in Feed (M_1)	Molar Fraction of NVC in Copolymer (m_1)	$m_1(n)\%$ ^a			$A_{230} : A_{238}$	
		$n = 1$	$n = 2$	$n \geq 3$	Experiment ^b	Calculated ^c
0.10	0.065	95.3	4.5	0.2	—	—
0.20	0.129	90.1	8.9	1.0	—	—
0.30	0.212	84.1	13.4	2.5	0.96	0.90
0.40	0.262	77.3	17.5	5.2	0.97	0.92
0.50	0.348	69.4	21.2	9.4	0.97	0.95
0.60	0.426	60.2	24.0	15.8	1.00	0.99
0.70	0.556	49.3	25.0	25.7	1.00	1.02
0.80	0.677	36.2	23.1	40.7	1.04	1.08
0.90	0.811	20.1	16.1	63.8	1.16	1.13

^a % Molar fraction of NVC in a sequence of n .

^b Ratio of the UV absorption of copolymers at 230 and 238 nm.

^c Ratio calculated on the basis of % molar fraction of isolated ($n = 1$) and interacted ($n \geq 2$) NVC units of copolymer and the value of ratio $A_{230} : A_{238}$ of *N*-isopropyl-carbazole (0.84)²⁹ and of PNVC (1.21).

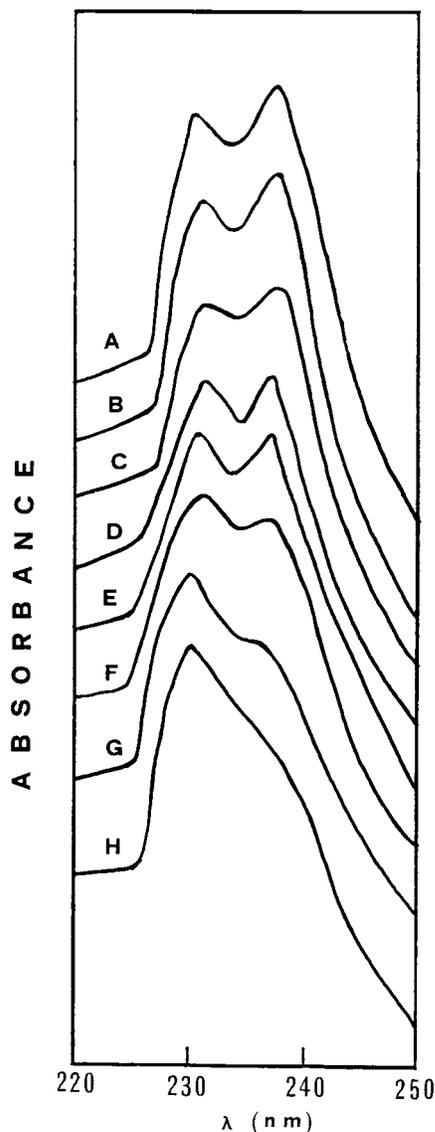


Figure 3 UV spectra in CH_2Cl_2 of NVC/DMAEMA copolymer samples having different content (mol %) of NVC units: (A) 21.2; (B) 26.2; (C) 34.8; (D) 42.6; (E) 55.6; (F) 67.7; (G) 81.1; (H) poly(*N*-vinylcarbazole).

for each copolymer was calculated. The relatively good agreement of these values with those experimentally determined by UV spectroscopy (Table III) shows that the determined reactivity ratios describe sufficiently well the distribution of comonomeric units in the copolymers.

The microstructure of the prepared copolymers was also studied by $^1\text{H-NMR}$ spectroscopy. The $^1\text{H-NMR}$ spectrum of PNVC shows in the region of aromatic (9–5 ppm) four signals at 7.7, 7.0, 6.3, and 4.8 ppm (Fig. 4). The first signals at 7.7 and 7.0 ppm are typical of the isolated carbazole units, while the last two are attributed to carbazole pro-

tons which are strongly shielded due to the overlap with a neighbor carbazole unit.^{17,29,30} In the $^1\text{H-NMR}$ spectrum of NIPC which contains only isolated carbazole units, only the first two peaks are present.³⁰

The $^1\text{H-NMR}$ spectra of all the prepared copolymers showed two peaks at 7.8 and 7.1 ppm. The copolymer with the highest content of NVC units (81.1 mol %) showed also a shoulder at around 6.3 ppm, indicating the occurrence of slight interactions between neighboring carbazole units. No peak at 4.8 ppm was observed (Fig. 4). It has been reported³¹ that the presence of this peak in the spectrum of a copolymer of NVC is indicative of the presence of NVC sequences at least five units long. From the determined values of r_1 and r_2 , the content of the above copolymer in NVC pentads ($n = 5$) was calculated to be 8.2 mol %. This result shows that the strong shielding of carbazole units responsible for the peak at 4.8 ppm is most probably encountered only when carbazole units are present in much longer sequences.

Physical Properties of Copolymers

Copolymers of NVC–DMAEMA were also prepared at higher yields in order to have samples to study some physical properties, such as viscosity (η_{inh}), molecular weight (\bar{M}_n), and glass transition temperature (T_g) (Table IV).

The diagram of the variation of viscosity and molecular weight of copolymer with the NVC molar fraction in the monomer feed shows the presence of a maximum value (Figs. 5 and 6), which might support the existence of charge-transfer interactions between NVC and DMAEMA molecules, as noticed above. The extremal character of the curve describing the dependence of copolymerization rate or molecular weight on the monomer feed is one of the most commonly used criteria for the indirect confirmation of the existence of donor–acceptor interactions between comonomers during copolymerization.³² Moreover, it is noteworthy that the maximum value of η_{inh} and \bar{M}_n seems to be reached for a molar fraction of NVC in the feed of about 0.75–0.80, which is rather close to the molar fraction of NVC that gives the maximum value of the run number (R) as it can be deduced from Figure 2.

Thermal Behavior of Copolymers NVC–DMAEMA

The glass transition temperature (T_g) of the prepared copolymers is presented in Table IV, and the variation of T_g with the composition of copoly-

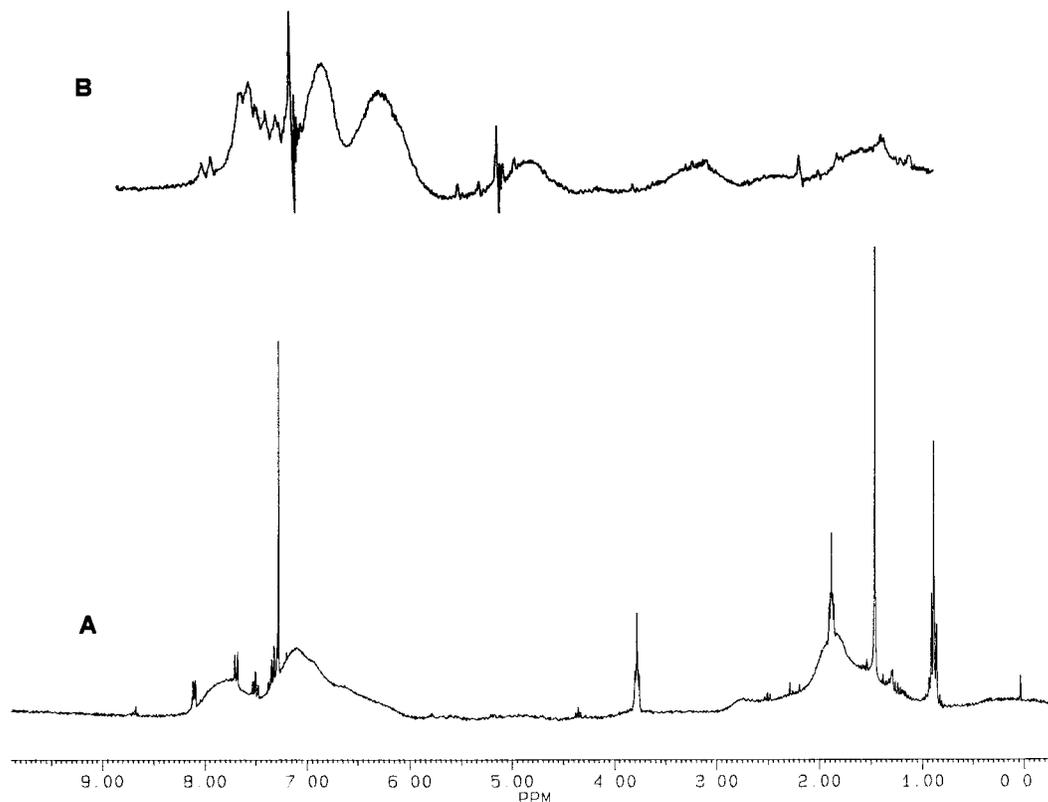


Figure 4 $^1\text{H-NMR}$ spectrum in $\text{CHCl}_3\text{-}d$ of copolymer NVC/DMAEMA having 81.1 mol % of (A) NVC units and (B) of poly(*N*-vinylcarbazole).

mer, in Figure 7. PNVC prepared in our lab, under the same conditions as for the copolymers, showed a T_g at about 212°C . The limiting literature⁷ value of the T_g of PNVC at high molecular weight is $\approx 227^\circ\text{C}$ but it is decreased with decrease of the molecular weight and the presence of a monomer

or other impurities. The T_g of PDMAEMA is reported¹³ to be 19°C . However, the T_g of PDMAEMA prepared in our lab showed a higher T_g at 34°C .

The T_g of copolymers showed a monotonic decrease as the % weight fraction of DMAEMA in

Table IV Physical Properties of NVC–DMAEMA Copolymers

Molar Fraction of NVC in Feed (M_1)	Conversion (Wt %)	η_{inh}^a (dL/g)	\bar{M}_n^b	T_g (K)	
				Expt ^c	Predicted ^d
0.10	18.4	0.44	120,000	—	—
0.20	18.1	0.45	124,000	316	325
0.40	18.5	0.47	148,000	332	345
0.50	17.8	0.50	162,000	340	359
0.60	17.2	0.53	174,000	346	372
0.70	18.7	0.58	178,200	365	395
0.80	16.9	0.63	186,700	378	417
0.90	19.1	0.42	140,600	403	444
1.00	19.2	0.25	76,800	485	—

^a Determined in solution in THF ($c = 0.5\%$) at 25°C .

^b Determined by membrane osmometer in THF solutions at 37°C .

^c Determined by DSC.

^d Predicted by the Fox equation.

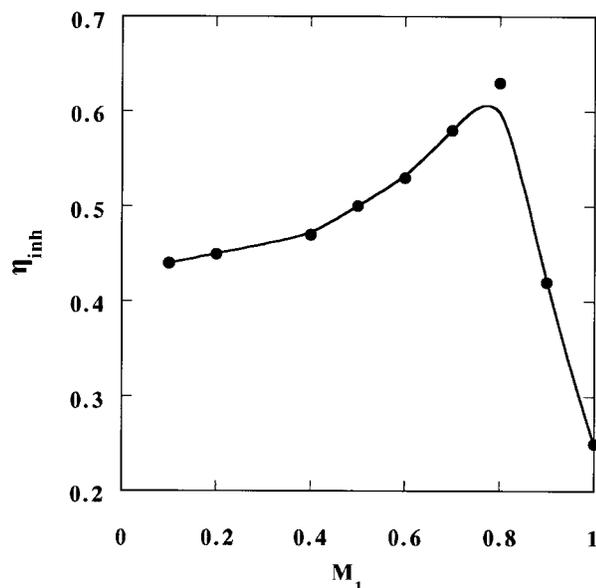


Figure 5 Dependence of inherent viscosity (η_{inh}) of the NVC/DMAEMA copolymers on the monomer feed composition; M_1 , molar fraction of NVC.

the copolymer increases. The copolymer with the lowest content in DMAEMA monomeric units (18.9 mol % = 15.9 wt %) showed a T_g at 130°C, i.e., 82°C lower than the T_g of PNVC (=212°C).

The experimental T_g values of copolymers do not agree with the theoretical values predicted by the well-known Fox equation. The latter in all

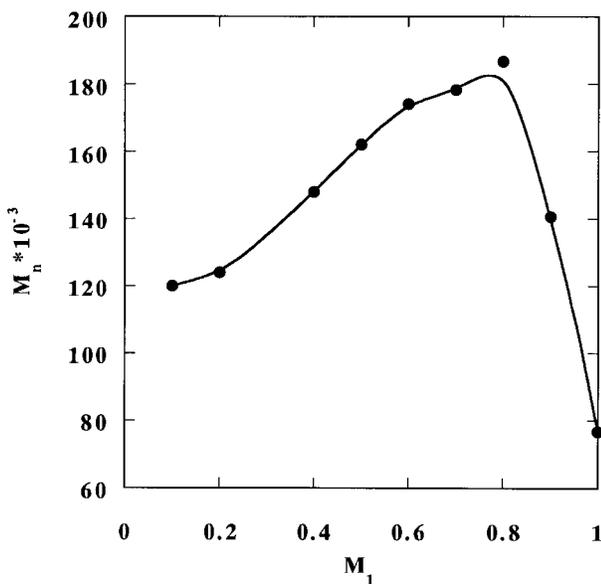


Figure 6 Dependence of number-average molecular weight (\bar{M}_n) of the NVC/DMAEMA copolymers on the monomer feed composition.

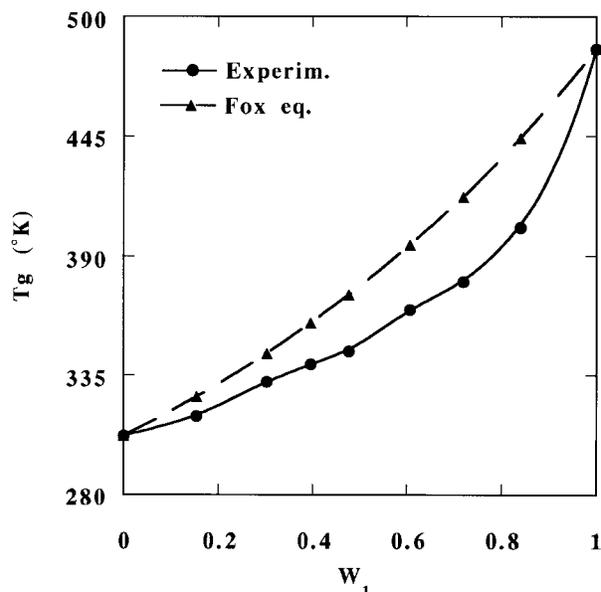


Figure 7 The experimental and the Fox equation predicted copolymer T_g 's values vs. the weight fraction of NVC in copolymer (W_1).

cases are higher than the former (Fig. 7). The Fox equation assumes that the freedom of rotation and free volume, contributed to a copolymer by a given monomer unit A , is the same as that it contributes to the homopolymer. However, this is not the case in all copolymers. The formation of diads with different monomer units (AB) results in new steric or polar interactions which may increase or decrease the T_g contribution of the A unit. Johnston,³³ using a T_{gAB}^* value for AB diads, proposed a new equation, which can be considered an extension of the pioneer work of Fox. San Roman et al.³⁴⁻³⁶ suggested a linear expression of Johnston's equation and used it for the assigning of T_{gAB}^* in a series of copolymers that they had prepared. The linear expression of Johnston's equation is

$$\begin{aligned} 1/T_g - (W_A P_{AA}/T_{gAA}) - (W_B P_{BB}/T_{gBB}) \\ = 1/T_{gAB}^* (W_A P_{AB} + W_B P_{BA}) \end{aligned}$$

where T_g is the copolymer glass transition temperature; T_{gAA} and T_{gBB} , the glass transitions of both homopolymers, and T_{gAB}^* , that of the alternating copolymer; W_A and W_B , the average weight fraction of monomer units in the copolymer; and P_{AA} , P_{BB} , P_{AB} , and P_{BA} , the first-order Markovian transition probabilities of having the corresponding linkages.^{35,36} Application of the above equation to our experimental values of T_g for NVC-

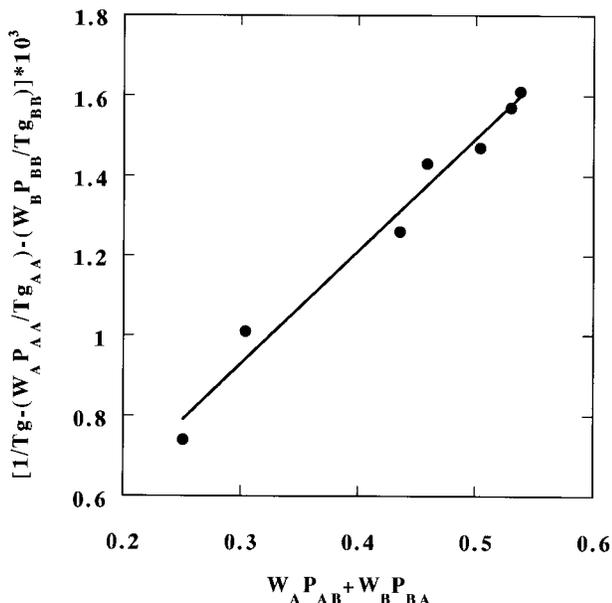


Figure 8 Application of the linearized expression of Johnston's equation to the copolymer system NVC/DMAEMA: (A) NVC; (B) DMAEMA.

DMAEMA copolymers showed good agreement (Fig. 8).

From the slope of the straight line, a value of $T_{gAB} = 83^\circ\text{C}$ ($A = \text{NVC}$, $B = \text{DMAEMA}$) was obtained, which is much lower than is the arithmetical average of T_g of both homopolymers [$\frac{1}{2}(T_{gA} + T_{gB}) = 123^\circ\text{C}$]. Thus, the alternating diad shows a higher flexibility than that expected from the combination of both monomeric units (NVC, DMAEMA) according to the T_g of the corresponding homopolymers. This result supports also the possible polar interactions between both monomer units.

Solubility of Copolymers NVC–DMAEMA

PNVC is soluble in solvents which are not friendly to the environment, such as toluene, dioxan, and THF. On the contrary, PDMAEMA is soluble in almost all organic solvents and in water. All the prepared copolymers are soluble in toluene, dioxan, THF, and also isopropyl alcohol and methyl ethyl ketone (MEK). They are swelled in ethanol. Their solubility increases with increase of DMAEMA content of the copolymer. Solutions of copolymers in MEK showed good film properties, especially those with a high content in DMAEMA. All copolymers were insoluble in water, even that with the highest content of DMAEMA (93.5 mol %), which, however, swelled in water.

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