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Synthesis and characterization of copolymers of *N*-vinylcarbazole and *N*,*N*-dimethylaminoethyl acrylate

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Abstract

Copolymers of *N*-vinylcarbazole (M_1) and *N*,*N*-dimethylaminoethyl acrylate (M_2) were prepared by free radical polymerization in toluene or DMF solution at 60°C, using 2,2′-azobisisobutyronitrile (AIBN) as initiator. The reactivity ratios of both the monomers were determined by the extended Kelen–Tüdös method and found to be $r_1 = 0.52 \pm 0.05$, $r_2 = 0.56 \pm 0.05$ (in toluene) and $r_1 = 0.44 \pm 0.04$, $r_2 = 0.18 \pm 0.03$ (in DMF). Copolymers prepared in toluene were also characterized by UV and ^{1}H-NMR sepctroscopy, viscosity and number- average molecular weight measurements and glass transition temperature determinations. The solvent effect on copolymer composition and microstructure is discussed. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: *N*-vinylcarbazole: *N*,*N*-dimethylaminoethyls acrylate; Solution-radical copolymerization; Reactivity ratios

1. Introduction

Poly(*N*-vinylcarbazole) (PNVC) has found much of academic and industrial interest because of its unusual electrical and photoelectrical properties, excellent thermal stability up to at least 300°C, ease of polymerization by a variety of techniques and intriguing morphological features [1,2]. It was used as a high-temperature dielectric material in the electric industry [3] and later as a photoconductor in electrophotography [4]. However, its extreme brittleness ($T_g = 227°C$) and poor mechanical and processing characteristics severely limited its commercial applications. In addition, the usual solvents for PNVC are tetrahydrofuran and toluene, which are not acceptable for use in the reprographics industry owing to pollution problem [5]. Attempts to improve the mechanical and processing characteristics of PNVC were focused on plasticization, orientation, blending and copolymerization. The copolymerization of NVC with vinyl monomers, such as alkyl acrylates or alkyl methacrylates, was studied by several investigators [6–14]. These monomers were found to act as internal plasticizers leading to products with better film properties [9,13]. Guthrie et al., have studied recently the copolymerization of NVC with acrylic and methacrylic acid in an effort to prepare alkali-soluble copolymers suitable for use as a part of a photoconductive lithographic printing plate assembly [5].

In our previous work we have studied the copolymerization of NVC with *N*,*N*-dimethylaminoethyl methacrylate [15,16] (DMAEMA) and the effect of the copolymerization solvent on the composition and microstructure of the copolymer [17]. This work is concerned with the synthesis and characterization of copolymers of NVC with *N*,*N*-dimethylaminoethyl acrylate (DMAEA). Copolymerization of NVC with alkylamino (meth)acrylates was found interesting, as these monomers are water-soluble and their homopolymers have low glass transition temperatures, especially the polyacrylates, and are soluble in water and in many organic solvents with very good film forming properties.

2. Experimental

2.1. Materials

NVC was supplied by Aldrich (98%, mp = 64°C–66°C) and recrystallized from methanol (mp = 65°C–66°C). DMAEA was supplied by Merck (> 99%) distilled at 67°C/12 mmHg before use and stored at 0°C. AIBN provided by Fluka (> 98%) was recrystallized from methanol (mp = 103°C–104°C). Toluene and DMF used

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Table 1
Copolymerization of NVC (M_1) with DMAEA (M_2) in toluene at 60°C

Conversion			Mean sequence length[a]		$m_1(n)$%[b]			A_{230}/A_{238}	
f_1[c]	(wt.%)	F_1[c]	$\bar{l}_1$	$\bar{l}_2$	$n=1$	$n=2$	$n\geq3$	Experim.[d]	Calcul.[e]
0.10	8.2	0.150	1.06	6.04	94.6	5.1	0.3	0.97	0.86
0.20	10.3	0.261	1.13	3.24	88.5	10.2	1.3	−	−
0.30	7.5	0.345	1.22	2.31	81.8	14.9	3.3	1.02	0.91
0.40	3.3	0.419	1.35	1.84	74.3	19.1	6.6	−	−
0.50	13.6	0.480	1.52	1.56	65.9	22.5	11.6	1.05	0.97
0.60	9.7	0.561	1.78	1.37	56.3	24.6	19.1	1.05	1.00
0.70	10.3	0.635	2.21	1.24	45.3	24.8	29.9	1.06	1.04
0.80	10.6	0.735	3.07	1.14	32.6	22.0	45.4	1.10	1.09
0.90	10.5	0.856	5.66	1.06	17.7	14.6	67.7	1.13	1.14

[a] $\bar{l}_1 = r_1([M_1/M_2]) + 1$ and $\bar{l}_2 = r_2([M_2/M_1]) + 1$.
[b] $\mathrm{cm}_1(n)$% = % molar fraction of NVC monomer units in a sequence of n.
[c] f_1=molar fraction of NVC in monomer feed; F_1=molar fraction of NVC in copolymer.
[d] Ratio of the UV absorption of copolymers at 230 and 238 nm.
[e] Ratio calculated on the basis of % molar fraction of isolated (n=1) and interacting (n=2) NVC units of copolymer and the value of ratio A_{230}/A_{238} of *N*-isopropylcarbazole (0.84)[27] and of PNVC (1.21).

as copolymerization solvents were analytical grade from Riedel-de Häen (99%) and used as received.

2.2. Copolymerization

All polymerizations were carried out in toluene or DMF solution at 60°C in glass tubes filled with nitrogen, using initial total comonomer concentration $1.00\ \mathrm{mol}\ 1^{-1}$ for toluene and $2.00\ \mathrm{mol}\ 1^{-1}$ for DMF, in the presence of AIBN (0.5 mol% to monomers). For each solvent nine copolymerizations were performed at various initial comonomer ratios expressed through the molar fraction of the first comonomer (f_1). For each initial comonomer ratio two copolymerizations were made and the average results of these experiments are shown the Table 1 and 2.

Polymerization time was about 60–80 min for solutions in toluene and 20–30 min for those in DMF. Copolymers prepared in toluene were isolated by pouring the polymerization solution into a large excess of cold petroleum ether (40°C–60°C) while those prepared in DMF in excess of diethyl ether were cooled with liquid nitrogen to about −60°C. Copolymers were purified by two precipitations from tetrahydrofuran into petroleum ether and dried in vacuo at 60°C to a constant weight.

2.3. Copolymer characterization

Copolymer compositions were evaluated by UV absorption spectroscopy, assuming the molar extinction coefficient per carbazole residue at 343 nm for PNVC does not vary with copolymer composition [11,18,19]. The extinction coefficient of the carbozolyl group in the PNVC prepared under the same experimental conditions as for the copolymers, was found to be $\epsilon = (2.612 \pm 0.182)$. $10^3\ \mathrm{dm}^3\ \mathrm{mol}^{-1}.\mathrm{cm}^{-1}$. UV spectra were taken in dichloromethane solutions, using a Hitachi U-2000 spectrophotometer.

^{1}H-NMR spectra were recorded on a Bruker 300-MHz

Table 2
Copolymerization of NVC (M_1) with DMAEA (M_2) in DMF at 60°C

Conversion			Mean sequence length[a]		$m_1(n)$[b]		
f_1[c]	(wt.%)	F_1[c]	$\bar{l}_1$	$\bar{l}_2$	$n = 1$	$n = 2$	$n \geq 3$
0.10	21.2	0.248	1.05	2.58	95.3	4.5	0.2
0.20	19.1	0.375	1.11	1.70	90.0	9.0	1.0
0.30	20.7	0.443	1.19	1.41	84.1	13.4	2.5
0.40	9.1	0.516	1.29	1.26	77.2	17.6	5.2
0.50	13.0	0.558	1.44	1.18	69.3	21.3	9.4
0.60	10.5	0.600	1.66	1.12	60.1	24.0	15.9
0.70	10.6	0.665	2.03	1.08	49.2	25.0	25.8
0.80	13.2	0.719	2.77	1.04	36.1	23.1	40.8
0.90	13.8	0.832	4.98	1.02	20.1	16.1	63.9

[a] $\bar{l}_1 = r_1([M_1/M_2]) + 1$ and $\bar{l}_2 = r_2([M_2/M_1]) + 1$.
[b] $m_1(n)$% = % molar fraction of NVC monomer units in a sequence of n.
[c] f_1 = molar fraction of NVC in monomer feed; F_1 = molar fraction of NVC in copolymer.

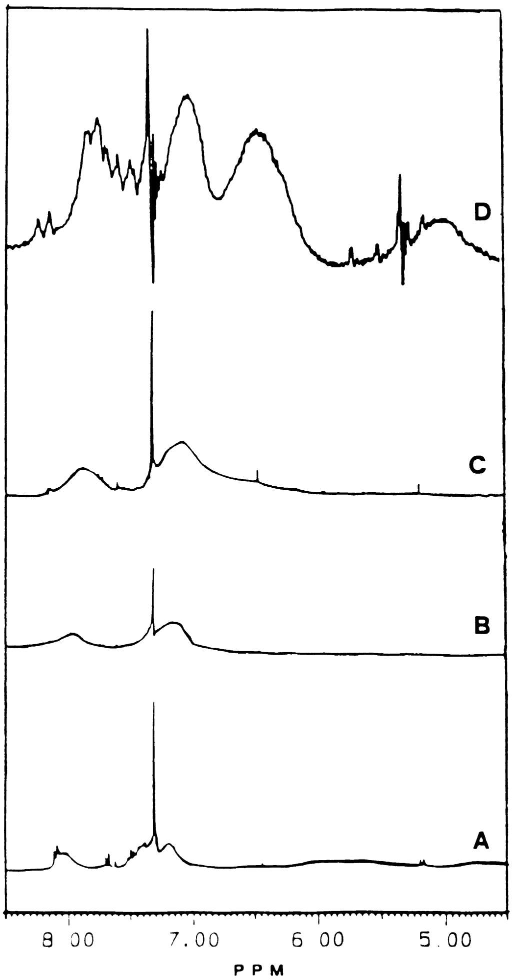

Fig. 1. ^{1}H-NMR spectra of copolymer NVC/DMAEA in $CHCl_3$-d solution: (A) sample containing 15.0 mol% of NVC units, (B) sample containing 48.0 mol% of NVC units, (C) sample containing 85.6 mol% of NVC units, (D) polyvinylcarbazole.

instrument, in $CDCl_3$ solutions and TMS as an internal standard. IR spectra were recorded on a Perkin–Elmer 297 spectrophotometer on KBr pellets. Viscosity measurements (η_{inh}) were performed with an Ubbelohde viscometer at 25°C in tetrahydrofuran ($c = 0.5\%$ w/v). Number-average molecular weight ($\bar{M}_n$) measurements were performed with 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.

3. Results and discussion

3.1. Synthesis and characterization

Copolymers of NVC and DMAEA were prepared under free-radical conditions in toluene at 60°C. The polymerization data and some properties of the copolymers are reported in Table 1. The crude copolymers obtained from monomer solutions rich in NVC were white powders, while those taken from solutions rich in DMAEA were colourless elastromers (with T_g lower than room temperature). They were characterized by IR and ^{1}H-NMR spectroscopy. Their spectra showed the occurrence of bands characteristic of both co-units. As NVC is known to polymerize cationically in the presence of electron acceptors, it was necessary to determine, if this process occurred with our monomer producing a mixture of homo PNVC and copolymer. DMAEA is an electron acceptor with a positive charge on its vinyl β-carbon atom ($e = +0.61$) [20]. The ^{1}H-NMR spectrum of the products showed that they were copolymers. PNVC has two exceptionally high field signals in the aromatic region of its ^{1}H-NMR spectrum as result of ring current interactions between adjacent carbazole units in the polymer [21]. These high field signals were absent in the copolymers synthesized here, as was also true in the case of NVC/DMAEMA copolymers [15,16] (see Fig. 2 and comments below referred to it).

All copolymers were soluble in toluene, dioxan, tetrahydrofuran, chloroform and dichloroethane, which are good solvents for homopolymers, PNVC and PDMAEA. Copolymers were also soluble in methylethyl ketone and those with high content in DMAEA units ($\geq$ 74 mol%) were soluble also in methanol and ethanol. These three solvents only for PDMAEA. The copolymers were insoluble in water even those with the highest content in DMAEA units (85.6 mol%)

The composition curve of NVC/DMAEA copolymers is presented in Fig. 2. In the same figure is also presented the composition curve of NVC/DMAEMA copolymers prepared in our previous work [16] under the same experimental conditions as copolymers NVC/DMAEA.

The former system shows an azeotropic point at 45/65 (NVC/DMAEA) feed composition, whereas in the latter the NVC/DMAEMA molar ratio is always lower in copolymer than in the monomer feed. Such a difference was also observed in copolymerization of NVC with methyl acrylate and methyl methacrylate [7] and NVC with (−) menthyl acrylate and (−) menthyl methacrylate [12]. In all cases the methacrylate displays a higher reactivity than acrylate, owing to the different resonance reactivity Q and polarity e of the two monomers. Methacrylates generally shows higher values of Q and lower values of e (Table 3), because of the presence of the methyl group at their vinyl β-carbon atom.

Reactivity ratios of NVC and DMAEA determined in terms of the data of Table 1 according to the Kelen–Tüdös procedure [24,25] are $r_1 = 0.52 \pm 0.05$ and $r_2 = 0.56 \pm 0.05$. The fact that both values are considerably lower than unity indicates the tendency of the monomers toward alternation in the copolymerization, owing to their opposite polarities. Reactivity ratios of NVC and DMAEA were also calculated by using the Alfrey–Price equations

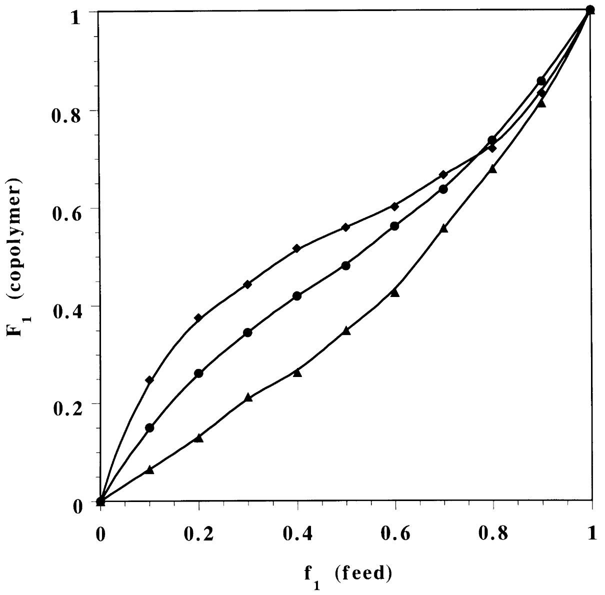

Fig. 2. Dependence of the molar fraction of NVC in copolymer (F_1) on the molar fraction of NVC in feed (f_1) in the copolymerization of NVC/DMAEA in toluene (●) and DMF (◆) and of NVC/DMAEMA (▲) in toluene at 60°C.

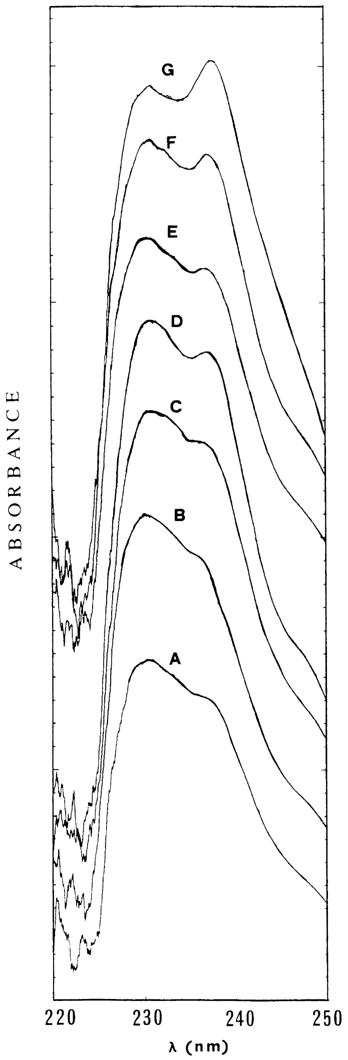

Fig. 3. UV spectra in CH_2Cl_2 of NVC/DMAEA copolymers with different content of NVC units (mol%): (A) 85.6; (B) 73.5; (C) 63.5; (D) 56.1; (E) 48.0; (F) 34.5; (G) 15.0.

and the Q and e values of the monomers (Table 3) and found to be $r_1 = 0.04$ and $r_2 = 0.65$. A discrepancy between the calculated and experimentally determined values of r_1 and r_2 is observed, which is especially significant for r_1. This discrepancy might suggest the existence of some interactions between monomers and/or macroradicals, which change the Q and e parameters. It is known that the product of reactivity ratios depends only on the difference in polarity for the two monomers ($r_1r_2 = \exp[-(e_1 - e_2)^2]$); the higher the difference in polarity, the lower the value of product. The experimental product ($r_1r_2 = 0.29$) is about ten times higher than the theoretical ($r_1r_2 = 0.03$) revealing a much lower difference in polarity of monomers than that theoretically expected. An analogous effect on the polarity was also observed in the monomer pair NVC/DMAEMA studied in our previous work [16] and in the pair of *N*-vinyl-2-pyrrolidone (NVP)/methyl methacrylate (MMA) studied by Czerwinski [26]. Binary solutions of NVP and MMA examined by means of IR and NMR spectroscopy showed that the polarity of NVP decreases, while the polarity of MMA increases through the formation of an electron donor–acceptor complex [26]. It is noteworthy that the change in the polarity of NVP was markedly larger than that of MMA. However study of solutions of NVC/DMAEA and NVC/DMAEMA [15] by UV spectroscopy, did not show the existence of a charge transfer complex between these monomers, even after heating. Therefore, in these pairs of monomers polar and charge transfer interactions might probably exist, which however do not lead to true molecular complexes.

Table 3
Q and e values of NVC and some alkyl (meth) acrylates

Monomer	Q	e	Literature
NVC	0.26[a]	− 1.29[a]	[21,22]
DMAEA	0.54[b]	+ 0.61[b]	[20]
DMAEMA	0.66	+ 0.49	[23]
Methyl acrylate	0.45	+ 0.64	[21,22]
Methyl methacrylate	0.78	+ 0.40	[21,22]

[a] These values were determined by the linear least-square evaluation of the reactivity ratios of twelve different monomer pairs.

[b] These are based on the reactivity ratios determined in a copolymerization of DMAEA with styrene.

The discrepancy between the experimental and theoretical values of reactivity ratios of NVC and DMAEA, may be as a result of the penultimate unit effects on the radical reactivity, which are not taken into account in the *Q–e* scheme. Such effects, electronic and/or steric, were observed by several researchers [27,28] in some monomer

Table 4
Physical properties of NVC/DMAEA copolymers prepared in toluene at 60°C

Conversion		η_{inh}[a]		T_g(K)	
f_1[b]	(wt.%)	(dl/g)	$\bar{M}_n$[c]	Expt[d]	Predicted[e]
0.00	16.0	–	22000	234	–
0.10	19.4	0.16	37000	254	260
0.20	18.5	–	–	280	281
0.30	21.9	0.19	–	295	298
0.40	19.2	–	–	311	314
0.50	18.5	0.23	56600	325	328
0.60	18.0	0.29	77000	340	348
0.80	17.0	0.37	128000	–	–
0.90	16.8	0.36	114000	409	433
1.00	19.2	0.25	76800	485	–

[a] Determined in solution in THF ($c = 0.5\%$) at 25°C.
[b] $f_1 =$ molar fraction of NVC in monomer feed.
[c] Determined by membrane osmometer in THF solutions at 37°C.
[d] Determined by DSC.
[e] Predicted by the Fox equation.

pairs and appeared in the rate of copolymerization (implicit penultimate unit effect, IPUE) or both in the rate of copolymerization and monomer reactivity ratios (explicit penultimate unit effect, EPUE). In the first case of IPUE the copolymer composition conforms to the terminal model (Mayo–Lewis equation) but the reactivity ratios of monomers are governed by the penultimate unit effects in an implicit form. The type of penultimate unit effect occurred in a monomer pair depends mainly on the difference in the size of the two comonomers [28]. The styrene/acrylonitrile pair is one of the first and few systems studied that displays an EPUE, while the pairs of styrene/methyl methacrylate, styrene/ethyl acrylate, methyl methacrylate/vinyl acetate exhibit an IPUE. It is suggested [27,28] that the IPUE is a very general phenomenon appearing in the most monomer pairs, while the EPUE is expected to occur only in pairs in which there is a large difference in the size of the substituents of both comonomers.

The NVC/DMAEA system studied in this work and NVC/DMAEMA studied in our previous work [15–17] was found to follow, as far as the copolymer composition is concerned, the terminal model. However it is quite probable these monomer pairs exhibit an IPUE, which governs the reactivity ratios of monomers in an implicit form, and is responsible to some extent for the observed discrepancy between the theoretical and experimental values of reactivity ratios. The experimental value of the reactivity ratio of NVC ($r_1 = 0.52$) is about ten times higher than the corresponding theoretical ($r_1 = 0.04$). This result shows a lower tendency of macroradical ending at NVC units in reacting with DMAEA monomer, compared with that theoretically expected. The NVC-terminated radicals are nucleophilic; therefore when the electrophilic DMAEA unit is the penultimate unit, the rate of addition of the electrophilic DMAEA monomer might be decreased, compared with the same addition in the absence of penultimate unit effects.

The distribution of monomeric units of the prepared copolymers, in terms of mean sequence length and sequence length distribution, as computed on the basis of the determined reactivity ratios, is presented in Table 1. Both monomes show about the same tendency to alternancy.

The UV spectra of copolymers show in the region of 220–250 nm, two bands with maxima at 230 and 238 nm, respectively (Fig. 3). As already reported [12,29] the former is characteristic of the electronically interacting nearest-neighbour carbazole units, whereas the latter is typical of the isolated carbazole chromophore. The intensity of the maximum at 238 nm increases as the content of NVC units and correspondingly the mean sequence length of NVC units in the copolymers is decreased. In the copolymer containing 15% of NVC units, where according to the determined values of reactivity ratios about 95% of NVC units are isolated, the absorbance at 238 nm is larger than that at 230 nm (Table 1). In this Table is also presented the value of the ratio A_{230}:A_{238}, calculated from the percent molar fraction of isolated ($n = 1$) and interacting carbazole chromophores ($n \geq 2$) of copolymer and taking into account the value of this ratio in *N*-isopropylcarbazole [29] and PNVC. A good agreement of these values with those experimentally determined by UV spectroscopy is observed for copolymers containing NVC units higher than 50%. For copolymers with lower NVC content, while it was evaluated on the basis of the determined reactivity ratios, that the absorption and 238 nm should be higher than that at 230 nm, an opposite situation is observed; this peak becomes predominant only in copolymer with NVC content 15%. This fact might be owing to the existence of electronic interactions between and the non-nearest neighbour carbazole groups. Such interactions, between remote carbazole groups, were also observed in essentially alternating copolymers of NVC and menthylethylfumarate or dimenthylethylfumarate, studied by UV, ^{1}H-NMR and fluorescence emission spectroscopy [30].

It is noteworthy that in copolymer NVC/DMAEA (acrylate) containing 34.5% NVC units, with mean sequence length $\bar{l}_1 = 1.22$ and $\bar{l}_2 = 2.31$, where more than 80% of NVC units are isolated, the absorbance at 230 nm is larger than that at 238 nm; on contrary in copolymer NVC/DMAEMA (methacrylate) prepared in our previous work [16] containing 34.8% NVC, with $\bar{l}_1 = 1.44, \bar{l}_2 = 2.63$, and about 70% content of isolated NVC, the absorbance at 238 nm is predominant. The acrylate moiety seems to favor more the interactions between the remote NVC units than the bulky methacrylate.

The ^{1}H-NMR spectra of copolymer samples display in the region of aromatic proton resonance two peaks typical of the isolated carbazole nuclei [30–32]. In copolymer containing 15% NVC units, the peaks appear at 8.06 and 7.18 ppm, in copolymer with 48% NVC, at 7.9 and 7.8 ppm and in copolymer with 85.6% NVC, at 7.8 and 7.02 ppm

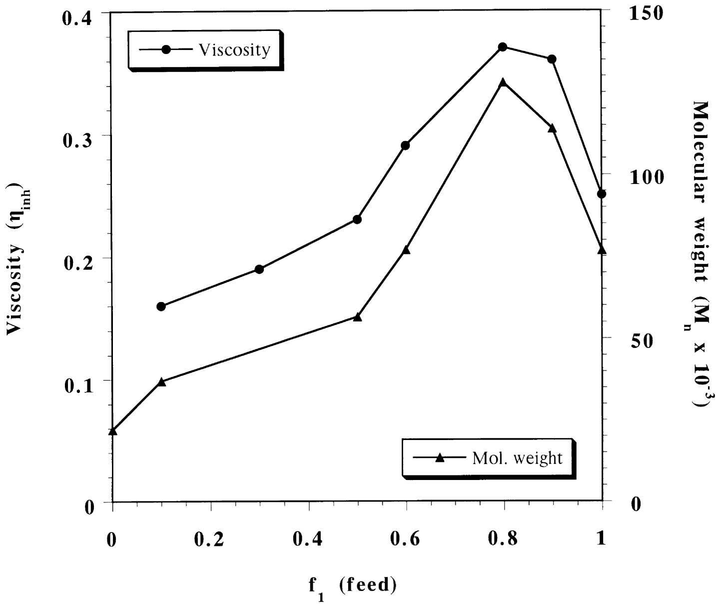

Fig. 4. Dependence of inherent viscosity (η_{inh}) and of number-average molecular weight ($\bar{M}_n$) of NVC/DMAEA copolymers on the molar fraction of NVC in feed (f_1).

(Fig. 1). This gradual upfield shift of the aromatic protons with increasing the NVC content is attributed [32] to cumulative shielding effects from neighboring NVC units. In copolymer with the highest content of NVC a shoulder also appears at around 6.4 ppm, indicating the occurrence in this sample of strong interactions between neighboring carbazole nuclei.

The ^{1}H-NMR spectra of PNVC and block copolymers derived from NVC, show in the aromatic region four signals at 7.7, 7.0, 6.3 and 4.8 ppm, while in the resonance spectra of carbazole and its *N*-substituted low molecular weight derivatives, only the first two signals are present. The signal at around 5.0 ppm corresponds to one proton in PNVC and is assigned to proton 1 of the benzene ring, shielded by adjacent NVC aromatic cones [32]. However in the spectrum of copolymer NVC/DMAEA with the highest content of NVC (85.6%) and a mean sequence length of NVC units longer than five ($\bar{l}_1 = 5.66$) no peak at 5.0 ppm was observed. It seems that only very long uninterrupted sequences of NVC units interact sufficiently to shield the proton 1.

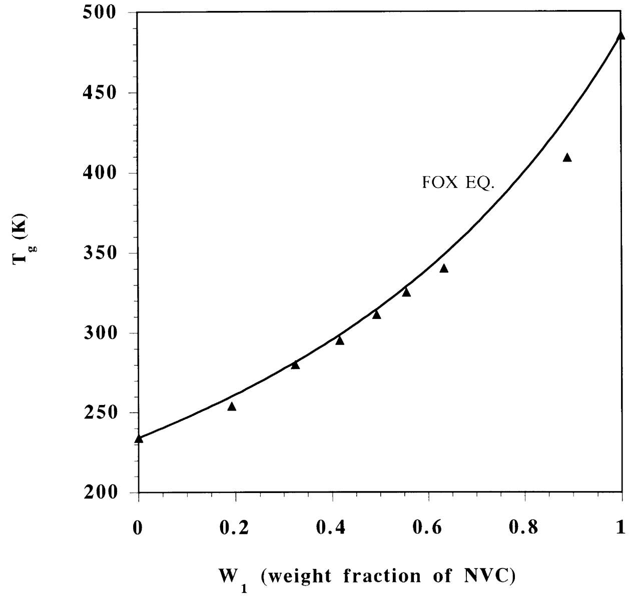

Fig. 5. The experimental and the Fox equation predicted copolymer T_g's values vs. the weight fraction of NVC in copolymer (W_1).

3.2. Physical properties

Copolymers of NVC/DMAEA were also prepared at higher yields and were characterized by determination of the inherent viscosity (η_{inh}), number average molecular weight ($\bar{M}_n$) and glass transition temperature (T_g) (Table 4). Fig. 4 shows the variation of η_{inh} and $\bar{M}_n$ with the NVC molar fraction in the monomer feed (M_1). The presence of a maximum in these curves, which also reveals the existence of a maximum in the curve describing the dependence of copolymerization rate on monomer feed, is a characteristic feature of the systems where donor–acceptor complexes participate in the chain propagation or there is a marked preference of comonomers for crosspropagation [33].

The observed maxima however lie not at equimolar monomer feed, but at feed richer in NVC at about 80/20. This monomer feed is rather close to the monomer feed 70/30 which gives copolymers with the maximum content of carbazole units in sequences of two ($m_1m_1m_2$) as can be deduced from the values of $m_1(n)$% in Table 1. These results show the existence of penultimate unit effects on the rate of copolymerization, as suggested previously.

The T_g values of the prepared copolymers showed a monotonic decrease as the % weight fraction of DMAEA unit in the copolymer increases (Fig. 5) following the well-known Fox equation $(1/T_{gp}) = (w_A/T_{gA}) + (w_B/T_{gB})$, where T_{gp} is the T_g of a copolymer containing weight fraction w_A and w_B of the monomer units A and B for which the homopolymers have glass transitions of T_{gA} and T_{gB}. The weight fraction of the monomer units in the copolymers was approximately considered equal with that of the corresponding copolymers prepared at lower conversions, and was calculated from the copolymer composition data given in Table 1. As far as the T_g values of homopolymers are concerned, the PNVC and PDMAEA prepared in our lab, showed a T_g at 212°C and -39°C correspondingly. The Fox equation suggests that the freedom of rotation and free volume contributed to a copolymer by a monomer unit is the same as it contributes to the homopolymer. It has to be noted that on the contrary to NVC/DMAEA copolymers, the NVC/DMAEMA copolymers studied in our previous work [16] followed as far as the dependence of T_g on the copolymer composition is concerned, the Johnson equation [34]. This equation takes into consideration the sequence distribution of the copolymer and assumes that the formation of AB dyads in copolymer results in new interactions (steric and/or polar) which increases or decreases the T_g distribution of the A unit. The determined T_g values of all NVC/DMAEMA copolymers were much lower than those predicted by Fox equation. That is the T_g contribution of the DMAEMA monomer unit to the copolymer T_g was lower than that to the sterically crowded homopolymer; on the contrary the contribution of DMAEA unit to the copolymer and homopolymer T_g was about the same.

3.3. Solvent effect on copolymer composition and microstructure

Copolymerization of NVC with DMAEA was also carried out in solution in DMF, which on the contrary to toluene is a strong polar and electron donor solvent, in order to study the solvent effect on reactivity ratios of monomers. The results obtained are presented in Table 2. All copolymers prepared in DMF in the region of monomer feed $f_1 < 0.7$ are richer in NVC units compared with the corresponding copolymers prepared in toluene.

The relationship of copolymer composition versus monomer feed composition for the two different solvents becomes more clear in Fig. 2. From the analytical data shown in Table 2 the reactivity ratios were calculated using the Kelen–Tüdös method [24,25], $r_1 = 0.44 \pm 0.04$ and $r_2 = 0.18 \pm 0.03$. These values are both lower than the corresponding ones obtained in toluene, especially the r_2, indicating a higher tendency of macroradicals to react with the unlike monomer. This result is also shown by comparing the reactivity ratio product r_1r_2 in the two solvents. In DMF it is much lower ($r_1r_2 = 0.08$) than that in toluene ($r_1r_2 = 0.29$).

The effect of solvent on the reactivity ratios of a series of monomers copolymerized by a free-radical mechanism was reviewed by Plochocka [35]. Changes in the reactivity ratios are attributed to: (a) electrostatic repulsion of charged monomers and radicals; (b) changes in monomer polarity; (c) participation of monomers in complexes; (d) hydrogen bonding of monomers with solvent and (e) solvent dielectric effects. Some years later Harwood [36] observed that in some free-radical copolymerizations the solvent does not effect the monomer and/or macroradical reactivity, but rather the comonomer ratio available for the growing chain, which is different from the global comonomer ratio, depending on the nature of the solvent. This kind of effect was called by Harwood the ‘‘bootstrap effect’’ and was recently quantitatively described by Klumperman et al. [37,38]. They suggest [38] that the bootstrap effect is determined mainly by the differences in the polarity between solvent and macroradical phase and also by donor–acceptor interactions between macroradicals and monomers or solvent.

In the present work toluene and DMF were used as solvents. DMF is a very polar ($\epsilon = 36.1$) and strong electron-donor solvent, on the contrary to toluene which is a non-polar ($\epsilon = 2.4$) and weak electron-donor solvent. However, the monomers used are both polar and NVC is an electron-donor, while DMAEA an electron acceptor. So DMF may affect the reactivity (Q) and polarity (e) of monomers and macroradicals and cause also differences in the local and global concentration of monomers, through polar and charge-transfer interactions. Hydrogen-bonding effects could not be observed in the studied system, as DMF and monomers are all proton acceptors.

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