

Copolymers of *N*-Vinylcarbazole and Ethyl Iodide Quarternized Dimethylaminoethyl Methacrylate

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ABSTRACT: Copolymers of *N*-vinylcarbazole (NVC) and the quarternary salt of *N,N*-dimethylaminoethyl methacrylate with ethyl iodide (DMAEMA·EI) were prepared by free-radical copolymerization in dimethyl sulfoxide at 70°C using α,α' -azobisisobutyronitrile (AIBN) as an initiator. The reactivity ratios of both monomers were determined according to the general copolymerization equation using the extended Kelen–Tüdös method and found to be $r_1 = 0.12 (\pm 0.04)$ and $r_2 = 0.84 (\pm 0.08)$. Copolymers were characterized by viscosity measurements and thermogravimetric analysis (TGA). Copolymers containing DMAEMA·EI higher than 60 mol % were water-soluble. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1517–1521, 1998

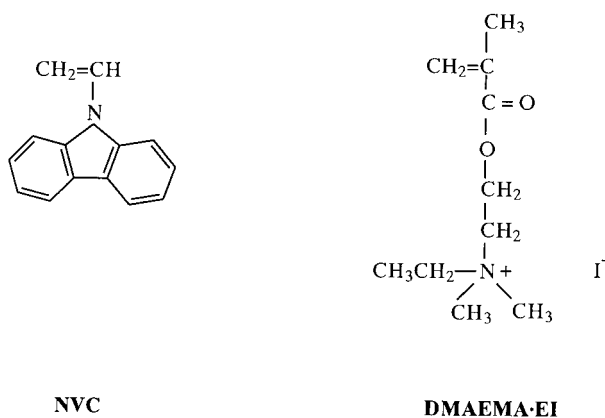
Key words: *N*-vinylcarbazole; solution-radical copolymerization; reactivity ratios

INTRODUCTION

Poly(*N*-vinylcarbazole) (PNVC) is a polymer of considerable academic and commercial 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 the reprographics industry.^{4,5} The development of water-soluble or dispersible 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 dispersible copolymers containing NVC monomer units were first prepared by Mulvaney and Chang.⁶

In an attempt to prepare water-soluble copolymers containing NVC, the copolymerization of NVC with *N,N*-dimethylaminoethyl methacrylate (DMAEMA), which is a water-soluble monomer, was studied in our previous work.^{7,8} The copolymers obtained, however, were insoluble in water and this even at the highest content of DMAEMA (93 mol %).

In this article, the copolymerization of NVC with the ethyl iodide salt of DMAEMA (DMAEMA·EI) which has a higher hydrophilic character than DMAEMA is studied:



EXPERIMENTAL

Reagents

N-Vinylcarbazole (NVC, from Aldrich, Steinheim, Germany) was recrystallized from methanol (mp

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Table I Copolymerization of NVC (M_1) and DMAEMA·EI (M_2) in DMSO at 70°C with AIBN (0.5 mol %) as the Initiator

Molar Fraction of NVC in Feed (M_1)	Conversion (wt %)	Molar Fraction of NVC in Copolymer (m_1)	Mean Sequence Length ^a		
			\bar{l}_1	\bar{l}_2	$\bar{l}_1 : \bar{l}_2$
0.10	11.5	0.104	1.01	8.56	1 : 9
0.20	7.8	0.180	1.03	4.36	1 : 4
0.30	6.8	0.264	1.05	2.96	1 : 3
0.40	3.5	0.336	1.08	2.26	1 : 2
0.50	5.7	0.396	1.12	1.84	1 : 2
0.60	16.2	0.446	1.18	1.56	1 : 2
0.70	9.0	0.489	1.28	1.36	1 : 1
0.80	4.5	0.569	1.48	1.21	1 : 1
0.90	12.8	0.654	2.08	1.09	2 : 1

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

65–66°C). *N,N*-Dimethylaminoethyl methacrylate (DMAEMA) (from Merck, Darmstadt, Germany, > 98%) was vacuum-distilled before use and stored at 0°C. Ethyl iodide was provided from Fluka, Buchs, Switzerland (>99%). α, α' -Azobisisobutyronitrile (AIBN, from Fluka) was recrystallized from methanol (mp 102–104°C). Dimethyl sulfoxide (DMSO) (puriss, from Merck) was used as the copolymerization solvent without further purification.

Synthesis of Ethyl Iodide Salt of DMAEMA

DMAEMA and an equivalent amount of ethyl iodide were stirred in acetone at 35°C for 24 h. After removal of acetone, the precipitated solid was taken by using dry ether and filtration. The solid was then dissolved in dry methanol, and the solution was made faintly cloudy by the addition of dry ether and stored at 0°C for 24 h. The white solid precipitated showed an mp = 101–102°C. ANAL: Calcd for $C_{12}H_{20}O_2NI$: C, 38.35%; H, 6.44%; N, 4.47%. Found: C, 38.14%; H, 6.29%; N, 4.28%.

Copolymerization

Copolymerization reactions were performed in glass tubes which were shaken in a 70°C water bath for 5–10 min. Solutions in DMSO were used with a total monomer concentration of 1.0 mol/L, while the ratio of the monomers was varied. The concentration of AIBN used as the initiator was 0.05 mol/L. Solutions were degassed by bubbling nitrogen for about 10 min. Copolymers were isolated by precipitation in cold acetone. Table I summarizes the results of these experiments. It is worth mentioning that before carrying out the co-

polymerizations preliminary experiments were done to establish that the heating of a solution of NVC, DMAEMA·EI, and AIBN in DMSO at 70°C led only to the formation of their copolymer and that no cationic homopolymerization of NVC was induced by probable acidic impurities present in the system or charge-transfer reactions with DMAEMA·EI. More details about the experiments done to confirm an analogous behavior for the pair NVC/DMAEMA were reported in our previous work.⁷

Copolymer Characterization

Copolymer compositions were evaluated by UV absorption spectroscopy, assuming the molar extinction coefficient per carbazole residue at 343 nm to be independent of the copolymer composition.^{9–11} UV measurements were performed in DMSO/DMAc (4/1 v/v) solutions in the spectral region 250–400 nm, using a Hitachi U-2000 spectrophotometer. The molar extinction coefficient of the carbazolyl group in the NVC homopolymer, prepared under the same experimental conditions as the copolymers, was found to be $\epsilon = 3.0 \times 10^3 M^{-1} \text{ cm}^{-1}$ (in a DMSO/DMAc 4/1 v/v solution). Then, the absorbance values at 343 nm of the copolymer solutions with known concentrations were determined and the wt % values of NVC in the copolymers were calculated. These were converted to mol % using the molecular weights of the monomers.

IR spectra were recorded on a Perkin–Elmer 281B spectrophotometer in thin films cast by slow evaporation of the solvent (DMSO) from the polymer solution. Viscosity measurements were per-

formed by an Ubbelohde viscometer at 25°C. The inherent viscosity of the copolymers (η_{inh}) was measured in DMSO solutions ($c = 0.5\%$ w/v). The reduced viscosity ($\eta_{sp/c}$) of the copolymer prepared from a monomer feed 10/90 (NVC/DMAEMA·EI) was measured in DMSO, water, and a 0.1N KBr aqueous solution. Thermogravimetric analysis (TGA) was carried out using a Perkin-Elmer thermobalance (TG-2) in a nitrogen atmosphere at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

Copolymers of NVC (M_1) with the ethyl iodide salt of *N,N*-dimethylaminoethyl methacrylate (DMAEMA·EI; M_2) were prepared under free-radical conditions in dimethyl sulfoxide (DMSO) at 70°C. The polymerization data and some properties of the copolymers are reported in Table I. Copolymers prepared from monomer solutions rich in NVC were white powders, while those prepared from solutions rich in DMAEMA·EI were transparent hard films.

From the analytical data shown in Table I, the reactivity ratios r_1 and r_2 were calculated using the extended Kelen-Tüdös (K-T) linearization method.¹² We preferred to use this method rather than the original K-T method, because the conversions of comonomers were not all low and extended up to 16.2%. The original K-T method is applicable only at sufficiently low conversions (5–10%), while the extended K-T method, taking into account also the percent weight conversion of the monomers, gives highly reliable results at high conversion data.¹² The 95% confidence limits of the determined r_1 and r_2 values were calculated using the equations proposed also by K-T.¹³ The determined reactivity ratios were

$$r_1 = 0.12 \pm 0.04 \quad r_2 = 0.84 \pm 0.08 \quad (r_1 r_2 = 0.10)$$

Since both reactivity ratios are less than unity and their product close to zero, a strong alternation tendency is indicated. This result is in agreement with considerations of polar effects for this monomer pair, since the e value for NVC is negative and that for ammonium iodide monomer is positive. The composition curve for the copolymer prepared is given in Figure 1. It shows an azeotropic point at a 10/90 monomer feed composition. Above this composition, NVC displays a lower reactivity than that of DMAEMA·EI.

A comparison of the above reactivity ratios of NVC and DMAEMA·EI, determined in a polar

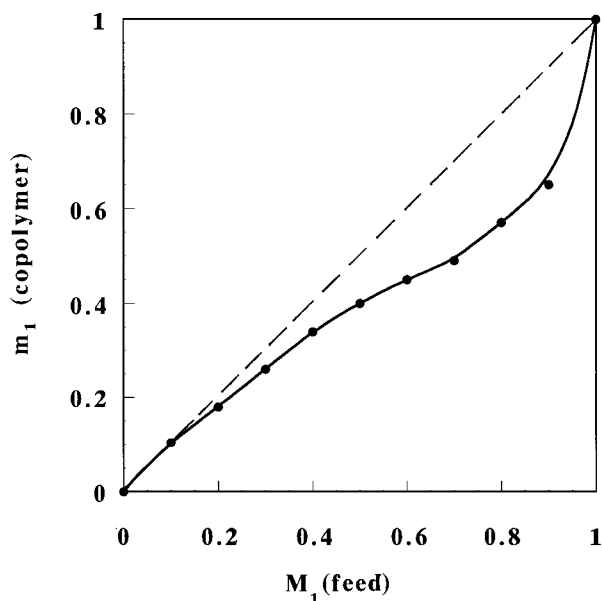


Figure 1 Relationship of the molar fraction of NVC in the feed (M_1) and the molar fraction in the copolymer (m_1) when NVC and the ethyl iodide salt of DMAEMA·EI are copolymerized at 70°C in DMSO.

solvent (DMSO, $\epsilon = 45.0$), with those of NVC and DMAEMA, ($r_1 = 0.10 \pm 0.02$ and $r_2 = 0.88 \pm 0.04$) determined also in a polar solvent (DMF, $\epsilon = 36.1$) in a previous work,¹⁴ shows no significant differences. This indicates that the quarternation of the amino group does not affect the reactivity of the vinyl group, probably because of the long distance between the amino and vinyl groups. An analogous behavior was also observed by Tanaka¹⁵ in the copolymerization of acrylamide with alkylaminoalkyl methacrylates or their quarternary salts.

In an attempt to take a look at the microstructure of the prepared copolymers, the mean sequence lengths of the monomer units (\bar{l}_1 and \bar{l}_2) were calculated from the determined values of the reactivity ratios (Table I). In the copolymer prepared from a monomer feed $[M_1]/[M_2] = 10/90$, each copolymer segment with M_2 units is approximately nine times longer than its adjoining segment with M_1 units. This rather large difference between \bar{l}_1 and \bar{l}_2 values is reduced considerably when moving from lower to higher M_1 feeds and leading to $\bar{l}_1 \approx \bar{l}_2$ at monomer feed $[M_1]/[M_2] = 70/30$. At this feed, about equal amounts of both monomers are incorporated into the copolymer and these are distributed with an alternating manner, which may be expressed as $-M_1M_2-$.

Another parameter, which also provides a useful picture of the sequence distribution in a copol-

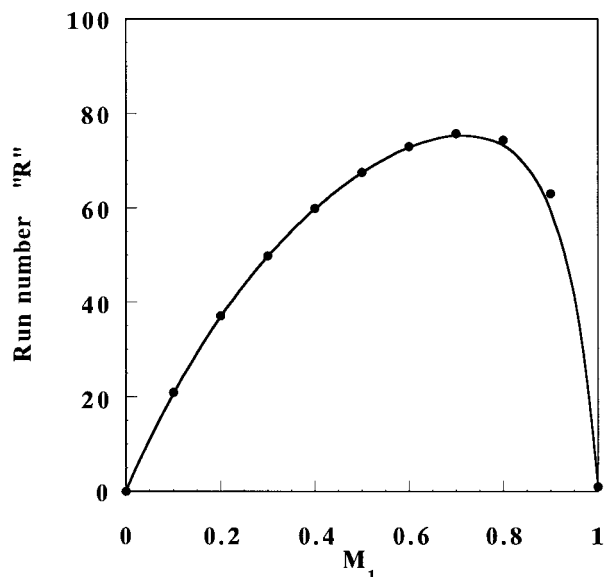


Figure 2 Variation of the "run number" (R) of the copolymer NVC/DMAEMA·EI with the monomer feed composition. M_1 , molar fraction of NVC.

mer chain and can be used to estimate the variation of the physical properties of copolymers with the composition, is the "run number" (R). It is defined as the average number of monomer alternations in a copolymer per 100 monomer units. Figure 2 shows the variation of " R " of the prepared copolymers with the molar fraction of NVC in the monomer feed. The maximum value of R

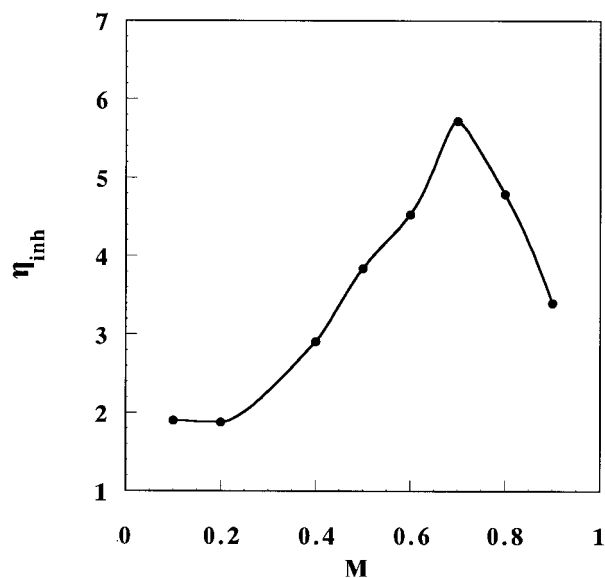


Figure 3 Dependence of the inherent viscosity (η_{inh}) of the NVC/DMAEMA·EI copolymers on the monomer feed composition. M_1 , molar fraction of NVC.

Table II Solubility of Quarternary Copolymers NVC/DMAEMA·EI

NVC in Copolymer (mol %)	DMSO	DMAc	Water
10.4	+	-	+
18.0	+	-	+
26.4	+	-	+
33.6	+	++	+
39.6	+	++	++
44.6	+	++	-
48.9	+	++	-
56.9	+	++	-
65.4	++	++	-

(+) Soluble; (++) soluble upon heating; (-) insoluble.

= 76 is reached for a molar fraction of NVC in the feed of about 0.70.

The prepared copolymers were characterized by IR spectroscopy. The spectra showed the characteristic bands of both monomer units, at 1740 cm^{-1} (C=O), 1620 , and 1590 cm^{-1} (aromatic C—C, C—N) and 750 and 725 cm^{-1} (aromatic C—H). The relative intensity of the bands due to different monomer units was different, depending on the composition of the copolymer.

The copolymers were also characterized by viscosity measurements in DMSO solutions ($c = 0.5\%$ w/v) at 25°C . The dependence of the viscosity on the composition of the copolymer is shown in Figure 3. It is noteworthy that a maxi-

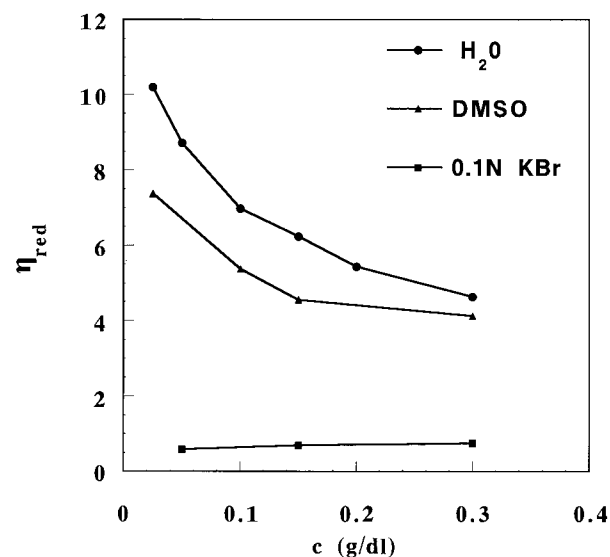


Figure 4 Reduced viscosity plots for the copolymer prepared from a monomer feed 10/90, measured in water, DMSO, and 0.1N KBr at 25°C .

Table III Data of Thermogravimetric Analysis of Copolymers NVC/DMAEMA · EI

NVC in Copolymer (mol %)	First Stage		Second Stage	
	T_m^a (°C)	Weight Loss (%)	T_m^a (°C)	Weight Loss (%)
10.4	278	67	426	25
18.0	290	60	458	30
26.4	292	60	446	26
33.6	286	56	445	30
39.6	280	55	450	34
44.6	294	54	438	32
48.9	291	54	438	32
56.9	287	42	439	44
65.4	281	36	417	50
100.0	490	100	—	—

^a Temperature of weight loss with maximum rate.

imum value of the inherent viscosity (η_{inh}) is reached for a molar fraction of NVC in the feed of about 0.70. This value is close to the molar fraction of NVC necessary to reach the maximum value of the run number (**R**) (Fig. 2) and corresponds to the copolymer with about the same content of both monomer units and distribution very close to $-M_1M_2-$. The existence of a maximum value in the curve describing the dependence of η_{inh} versus monomer feed suggests the existence of specific interactions between both monomers, due to the difference in their polarity. An analogous behavior was also observed⁸ in the NVC/DMAEMA monomer pair.

All the copolymers were insoluble in most organic solvents and soluble only in DMSO or DMAc. Copolymers with a high content of the quarternary salt DMAEMA · EI moiety were also soluble in water (Table II).

The reduced viscosity (η_{sp}/c) plots of the copolymer prepared from a monomer feed of 10/90 are depicted in Figure 4. The viscosity in DMSO and water exhibits a concentration dependence analogous to that for polyelectrolytes. On the other hand, the copolymer in 0.1N KBr behaves as the uncharged polymers, as indicated by the linear plot in Figure 4.

The results of the thermogravimetric (TG) and derivative thermogravimetric analysis (DTG) of the prepared copolymers are summarized in Table III. All copolymers showed two steps of decomposition with a maximum rate at 280–290 and 420–

450°C. The decomposition of PNVC took place in one stage with a maximum rate at 490°C. It breaks up almost completely into the monomer through a stepwise unzipping mechanism.¹⁶ The thermal stability of the copolymers NVC/DMAEMA · EI was generally lower than that of the copolymers NVC/DMAEMA studied in our previous work.⁷ The latter showed also two steps of decomposition, but with a maximum rate at relatively higher temperatures, 335–356 and 445–477°C.

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