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Solvent effect on the free-radical copolymerization of N-vinylcarbazole with N,N-dimethylaminoethyl methacrylate

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The reactivity ratios of N-vinylcarbazole (r_1) and N,N-dimethylaminoethyl methacrylate (r_2) were determined at 60°C in toluene, dioxane, methylethyl ketone and N,N-dimethylformamide (DMF) solutions. The values calculated by the extended Kelen–Tüdös method were $r_1 = 0.44 \pm 0.05$, $r_2 = 1.63 \pm 0.10$ (in toluene), $r_1 = 0.32 \pm 0.05$, $r_2 = 1.34 \pm 0.10$ (in dioxane), $r_1 = 0.15 \pm 0.03$, $r_2 = 1.10 \pm 0.07$ (in methylethyl ketone) and $r_1 = 0.10 \pm 0.02$, $r_2 = 0.88 \pm 0.04$ (in DMF). There is a marked effect of solvent on both r_1 and r_2 in all these systems, which is most probably due to changes in the dielectric constant of the solvents used. © 1997 Elsevier Science Ltd.

(Keywords: N-vinylcarbazole; N,N-dimethylaminoethyl methacrylate; solution-radical copolymerization)

INTRODUCTION

It is well known that solvents often greatly influence the reactivity ratios of monomers in free-radical copolymerization[1]. Monomers susceptible to solvent effects are mainly ionogenic, hydrogen-bond forming or polar monomers. Changes in the reactivity ratios have been attributed to electrostatic forces, hydrogen bonding, polar–polar interactions and electron donor–acceptor complex formation[1]. Some of them, such as hydrogen bonding, polar or charge transfer interactions are not always easy to discern and in some copolymerizations operate simultaneously.

Harwood found that, in some solvent-sensitive copolymerization systems, solvent effects on the determined reactivity ratios are not manifested in the chain-end reactivity, but rather in differences in local monomer concentrations around the growing chain-end radicals and the global monomer concentrations[2]. This kind of effect has been called the 'bootstrap effect' by Harwood. It is observed in monomer pairs with relatively small difference in polarity, such as the styrene–methyl methacrylate pair[3,4].

In our previous work[5] we have studied the free-radical copolymerization of N-vinylcarbazole (NVC) with N,N-dimethylaminoethyl methacrylate (DMAEMA) initiated by α,α'-azobisisobutyronitrile (AIBN) in solution in tetrahydrofuran at 60°C. It was found that this copolymerization follows the simple terminal model of copolymerization and the reactivity ratios of monomers have been roughly evaluated. NVC is a polar, electron donating monomer characterized by a negative polarity of its vinyl bond ($e_1 = -1.29$)[6]. On the other hand DMAEMA is also a polar, but an electron acceptor monomer with a positive charge on its vinyl β-carbon atom ($e_1 = +0.49$)[7]. So in the solution copolymerization of these two monomers some solvent effects on the reactivity ratios could be observed.

This work is concerned with the radical copolymerization of NVC and DMAEMA in four solvents with different polarity and electron donating ability. The solvents used were toluene, dioxane, methylethyl ketone and DMF. All are non-proton donors and could not form hydrogen bonds with the monomers which are proton acceptors. These were chosen because they insured conditions of homogeneous solution copolymerization; both monomers and the resulting copolymer were soluble in these solvents.

EXPERIMENTAL

Materials

NVC was supplied by Aldrich (98%, mp = 64–66°C) and recrystallized from methanol (mp = 65–66°C). DMAEMA was supplied by Merck (> 98%) distilled at 83–84°C/18 mmHg before use and stored at 0°C. AIBN provided by Fluka (> 98%, mp = 102–104°C) was recrystallized from methanol (mp = 103–104°C). Toluene, dioxane, methylethyl ketone and DMF used as copolymerization solvents were analytical grade from Riedel–de Häen (99%) and used as received.

Copolymerization

All copolymerizations were conducted in glass tubes into which the required amounts of monomers, initiator and solvent were placed. The starting overall concentration of the two comonomers was 1.00 mol l^{-1} and that of initiator (AIBN) 0.005 mol l^{-1}. The polymerization solution was flushed with nitrogen for 2 min, then

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capped and placed in a shaking bath thermostated at 60°C for a certain time. Polymerizations in all solvents proceeded in homogeneous phase. Copolymers prepared in toluene, dioxane or methylethyl ketone were isolated from the polymerization solution by precipitation in a large amount of cold petroleum ether (40–60°C), while those prepared in DMF in excess of diethyl ether, cooled with liquid nitrogen to about −60°C. Copolymers were purified by two precipitation-dissolving cycles in tetrahydrofuran and petroleum ether. They were exhaustively dried under vacuum at 60°C to constant weight.

It is worth mentioning that before carrying out the copolymerizations, preliminary experiments had been done to establish that the heating of a solution of NVC, DMAEMA and AIBN in each of the studied solvents 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. More details about the experiments done to confirm this behaviour are reported in our previous work[5].

For each solvent nine copolymerizations were performed at various initial comonomer ratios expressed through the molar fraction of the first comonomer f_1 (*Tables 1* and *2*). For each initial copolymer ratio three copolymerizations were made and the average results of these experiments are shown in *Tables 1* and *2*. In all copolymerizations the reaction time was short enough (20–110 min) to obtain relatively low monomer conversions; the polymerization time increased with increasing the content of DMAEMA in the monomer feed in all solvents. Conversions were determined gravimetrically.

Copolymer composition was determined by u.v. 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 copolymer[8–10]. Absorption values at 343 nm obtained from u.v. spectra of NVC homopolymer solutions in dioxane with different concentrations were plotted against the concentration to give a value for $\epsilon = (2.861 \pm 0.189) \times 10^3\ \mathrm{dm^3\ mol^{-1} cm^{-1}}$.

RESULTS AND DISCUSSION

The radical copolymerization of NVC (M_1) with DMAEMA (M_2) was carried out in various solvents in the presence of AIBN (0.5 mol%) at 60°C. The copolymer compositions, as molar fraction of NVC, and the corresponding wt% conversions are shown in *Table 1* (toluene and dioxane) and *Table 2* (methylethyl ketone and DMF).

Table 1 Results of radical copolymerization of NVC (M_1) and DMAEMA (M_2) in toluene and dioxane solution

	Toluene		Dioxane	
f_1^a	Conversion (wt%)	F_1^b	Conversion (wt%)	F_1^b
0.10	12.3	0.065	12.0	0.080
0.20	5.7	0.129	11.2	0.144
0.30	16.9	0.212	13.6	0.223
0.40	4.5	0.262	13.6	0.278
0.50	7.9	0.348	8.0	0.364
0.60	8.1	0.426	14.9	0.454
0.70	14.4	0.556	5.6	0.524
0.80	14.1	0.677	7.0	0.652
0.90	10.8	0.811	17.0	0.795

Average results of three series of experiments for each initial monomer feed composition
[a] Molar fraction of NVC in monomer feed
[b] Molar fraction of NVC in copolymer

Table 2 Results of radical copolymerization of NVC (M_1) and DMAEMA (M_2) in methylethyl ketone and DMF solution

	Methylethyl ketone		DMF	
f_1^a	Conversion (wt%)	F_1^b	Conversion (wt%)	F_1^b
0.10	19.5	0.091	6.9	0.100
0.20	12.1	0.157	1.4	0.185
0.30	16.2	0.236	4.0	0.254
0.40	11.4	0.291	12.6	0.325
0.50	7.3	0.351	12.3	0.365
0.60	7.0	0.423	9.4	0.426
0.70	23.6	0.505	16.7	0.491
0.80	4.2	0.572	18.5	0.558
0.90	15.3	0.695	10.8	0.647

Average results of three series of experiments for each initial monomer feed composition
[a] Molar fraction of NVC in monomer feed
[b] Molar fraction of NVC in copolymer

It is shown that copolymers obtained from solutions with the same monomer feed but in different solvent have different composition. The greatest difference is observed for copolymers prepared in toluene and DMF. At $f_1 = 0.1$ copolymers prepared in toluene have the lowest content of NVC units, while at $f_1 = 0.9$ the highest. An opposite trend is observed for copolymers prepared in DMF. The solvent effect on copolymer composition is more clearly seen in *Figure 1*. The shape of the copolymerization diagram in DMF indicates an alternating character of the copolymerization, while in toluene the copolymerization is more random.

From the analytical data shown in *Tables 1* and *2*, the reactivity ratios r_1 and r_2 were calculated using the extended Kelen–Tüdös (K–T) linearization method[11]. 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 23.6%. The original K–T method is applicable only at sufficiently low conversions (5–10%) while the extended K–T method, also taking into account the wt% conversion of monomers, gives highly reliable results at high conversion data[11]. The 95% confidence limits of the determined r_1 and r_2 values were calculated using the equations also proposed by Kelen–Tüdös[12]. The obtained values of r_1 and r_2 are given in *Table 3*, together with two physicochemical parameters of copolymerization solvents. It is shown that both reactivity ratios and their product (r_1r_2) change with the copolymerization solvent. This result indicates that the observed changes in reactivity ratios are due to solvent effects on the reactivity of polymerization sites, i.e. double bonds and/or macroradicals, and not to a bootstrap effect; because in the latter case only the reactivity ratios change in various solvents, while the reactivity ratio product remains constant[14].

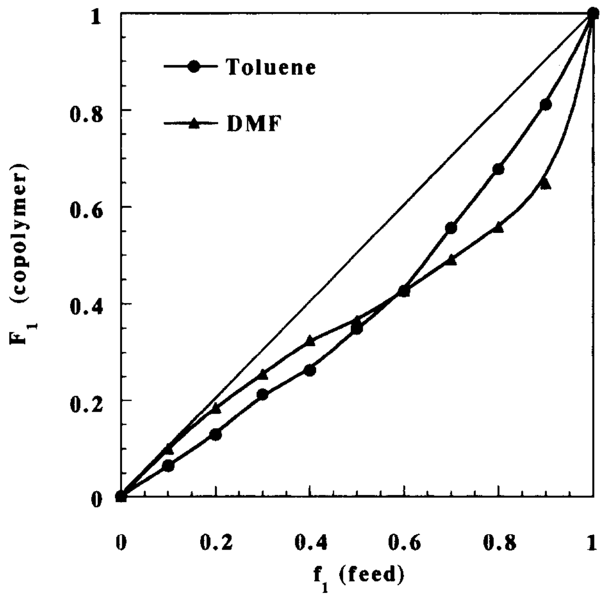

Figure 1 Dependence of the molar fraction of NVC in copolymer (F_1) on the molar fraction of NVC in feed (f_1) in the NVC–DMAEMA copolymerization in toluene and DMF

Table 3 Reactivity ratios of NVC (r_1) and DMAEMA (r_2) determined in various solvents at 60°C

Solvent	ϵ^a	$\Delta\nu_D^b$ (cm^{-1})	r_1	r_2	r_1r_2
Toluene	2.4	2	0.44 ± 0.05	1.63 ± 0.10	0.72
Dioxane	2.2	77	0.33 ± 0.05	1.34 ± 0.10	0.43
Methylethyl ketone	18.5	57	0.15 ± 0.03	1.10 ± 0.07	0.16
DMF	36.1	107	0.10 ± 0.02	0.88 ± 0.04	0.09

[a] Dielectric constant of solvent

[b] Measure of the electron-donating power of solvent taken from Kagiya *et al.*[13]. It is defined as the relative difference (counted as wave numbers) of the O–D or the C–D absorption band observed in the solvent, containing a small amount of methanol-*d*, from that in benzene, chosen as a reference compound. The greater the $\Delta\nu_D$ value, the stronger the electron-donating power of the solvent

The lower reactivity ratio of NVC ($r_1 = k_{11}/k_{12}$) in DMF ($r_1 = 0.10$) than that in toluene ($r_1 = 0.44$) could be due to a decrease of k_{11} and/or increase of k_{12}. Study of the solvent effect on the propagation rate constant of the homopolymerization of NVC has not been found in the literature. However, it is described[15] that N-vinylpyrrolidone (NVP), analogous to the NVC electron donor monomer, shows an increase to its propagation rate constant in polar solvents, due to solvation of NVP and poly-NVP macroradicals. Hence, in NVC–DMAEMA copolymerization in DMF, both constants k_{11} and k_{12} most probably increase, but the increase of the latter is more pronounced, so finally r_1 decreases.

The reactivity ratio of DMAEMA in toluene ($r_2 = 1.63$) shows that $k_{22} > k_{21}$, while in DMF ($r_2 = 0.88$) $k_{22} < k_{21}$. Literature data[16] on the homopolymerization of DMAEMA in various solvents describe an increase of $k_p = k_{22}$ in polar or proton-donor solvents. Thus the increase of k_{21} in polar DMF seems to be much higher than that of k_{22} and the poly-DMAEMA radical prefers to react with the unlike monomer.

The polarities of poly-NVC and poly-DMAEMA radicals are of opposite sign, so the observed higher preference of DMF to react with the unlike monomer must be due to a higher difference of their polarity in DMF than in toluene. This result is more clearly shown by comparing the values of the reactivity ratio products in these two solvents, because r_1r_2 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 r_1r_2. In DMF the determined value of $r_1r_2 (= 0.09)$ is much lower than that in toluene $r_1r_2 = 0.72$.

Dioxane is a non-polar solvent ($\epsilon = 2.2$) like toluene ($\epsilon = 2.4$). However the product r_1r_2 determined in dioxane was lower than that in toluene. This decrease may be explained if we suggest a charge-transfer interaction between dioxane and DMAEMA. Dioxane, contrary to toluene, is an electron-donor solvent (*Table 3*) which could interact with the electron-acceptor carbonyl group of DMAEMA. Such an interaction leads to an increase of the electron-acceptor properties of the carbonyl group and decrease in the electron density on the carbon atom of the CH$_2$=group conjugated with the carbonyl. Thus the difference in the polarities of NVC and DMAEMA would be higher in dioxane than in toluene, where no such charge-transfer interaction can take place.

Methylethyl ketone shows about the same electron-donor ability with dioxane but much higher polarity. Thus the lower values of reactivity ratios observed in methlethyl ketone than dioxane confirm the important role of solvent polarity in NVC–DMAEMA copolymerization.

In *Figure 2* the $1/r_1$ and $1/r_2$ values are plotted as a function of the solvent dielectric constant. The reactivity of both types of macroradicals towards the unlike monomer increases with increasing the solvent polarity. The increase, however, of $1/r_1$ with the solvent polarity is much higher than that of $1/r_2$. The poly-NVC radicals are more sensitive to solvent effects. The straight lines obtained in *Figure 2* indicate that the dielectric constant of solvent seems to be the major factor which determines the composition of the copolymer obtained from a given feed.

Solvent effect on copolymer microstructure

The microstructure of the prepared copolymers was examined on the basis of first-order Markov statistics.

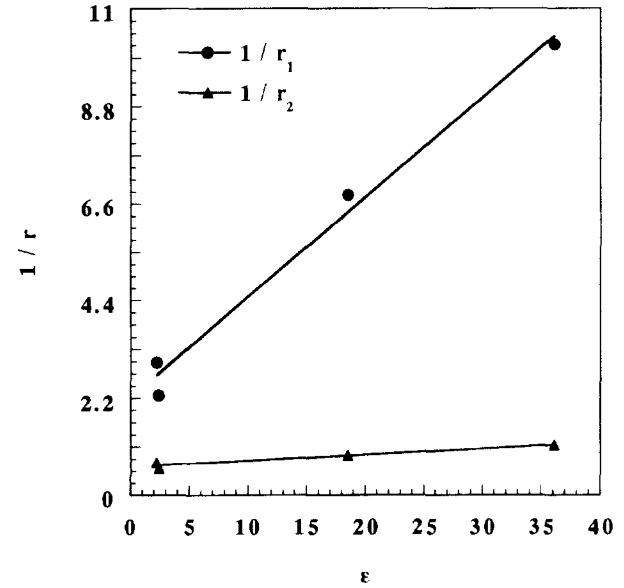

Figure 2 Dependence of relative reactivity of poly-NVC and poly-DMAEMA radicals towards DMAEMA and NVC monomers respectively, on the dielectric constant of the copolymerization solvent

Taking into account well-known statistical relations and the determined values of reactivity ratios two statistical parameters were calculated: the 'run number' (R) and the number-average sequence length of the monomer units ($\bar{l}_1$, $\bar{l}_2$). They both describe the distribution of the monomer units in a copolymer.

The run number has been defined by Harwood[17] as the average number of sequences of either type of monomers per 100 monomer units. In an alternating copolymer $R = 100$ and in a homopolymer $R = 1$. So the higher the value of R in a copolymer, the higher the tendency of its monomer units for alternation. The dependence of 'R' with the monomer feed for copolymers prepared in each one of the four solvents used is shown in *Figure 3*. The maximum value of 'R' increases in the order: toluene ($R = 54$) < dioxane (59) < methylethyl ketone (71) < DMF (77). The monomer feed at which the R_{max} is observed also increases in the same order.

The value of 'R' is given by the equation $R = 200/(\bar{l}_1 + \bar{l}_2)$; so the value of R_{max} corresponds to the minimum value of the sum $(\bar{l}_1 + \bar{l}_2)$. The calculated number-average sequence lengths of NVC ($\bar{l}_1$) and DMAEMA ($\bar{l}_2$) units in copolymers prepared in toluene

Table 4 Number average sequence lengths of monomer units in copolymers NVC–DMAEMA, prepared in toluene and DMF; $\bar{l}_1$ (NVC), $\bar{l}_2$ (DMAEMA)

	Toluene			DMF		
f_1 (NVC) (feed)	$\bar{l}_1$	$\bar{l}_2$	$\bar{l}_1/\bar{l}_2$	$\bar{l}_1$	$\bar{l}_2$	$\bar{l}_1/\bar{l}_2$
0.10	1.049	15.688	0.067	1.011	8.947	0.113
0.20	1.110	7.528	0.146	1.024	4.532	0.226
0.30	1.189	4.808	0.247	1.042	3.060	0.341
0.40	1.294	3.448	0.375	1.065	2.324	0.458
0.50	1.441	2.632	0.547	1.098	1.883	0.583
0.60	1.662	2.088	0.796	1.147	1.589	0.722
0.70	2.029	1.699	1.194	1.229	1.378	0.892
0.80	2.764	1.408	1.963	1.392	1.221	1.140
0.90	4.969	1.181	4.207	1.882	1.098	1.714

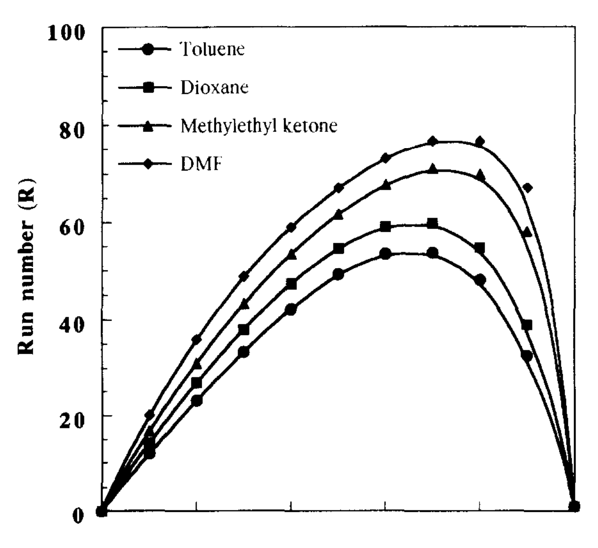

Figure 3 Variation of the 'run number' (R) of copolymer with the monomer feed composition (f_1)

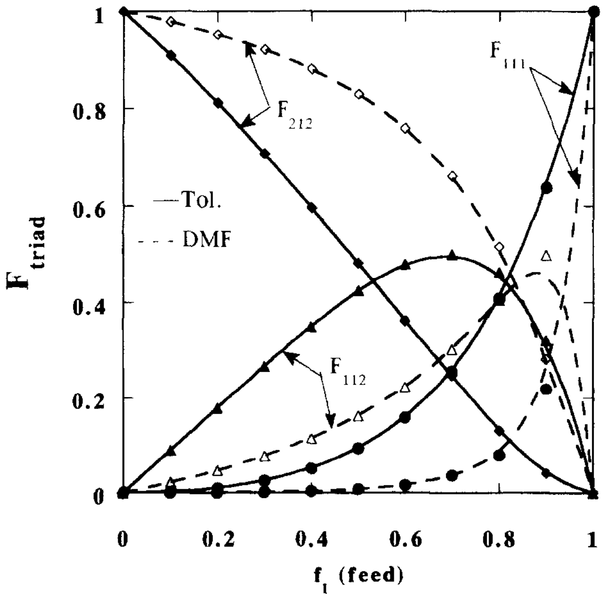

Figure 4 The molar fraction of NVC centred triads, calculated from statistical considerations vs molar fraction of NVC in the monomer feed (f_1)

and DMF, which showed the greatest difference in composition, are shown in *Table 4*.

Significant differences exist between the $\bar{l}_1$ and $\bar{l}_2$ for copolymers prepared from a monomer feed of $f_1 = 0.10$ in a different solvent. In toluene each segment with DMAEMA units are approximately sixteen times longer than its adjoining segment with NVC units, while in DMF the segment with DMAEMA units is only nine times longer than the NVC segment. This rather large difference between the values of lengths is considerably reduced in the range of a monomer feed of $f_1 = 0.50$–0.60. Copolymers prepared from a feed of $f_1 = 0.50$ either in toluene or DMF have about the same composition. The ratio of sequence lengths $x = \bar{l}_1/\bar{l}_2$, which theoretically corresponds to the ratio of the molar fractions of comonomers in copolymer (F_1/F_2), is $x_1 = 0.55$ in the case of toluene, which is very close to $x_2 = 0.58$ for DMF (*Table 4*). The ratio x_1/x_2 ($= 0.94$) for this monomer feed is closer to unity than any other feed.

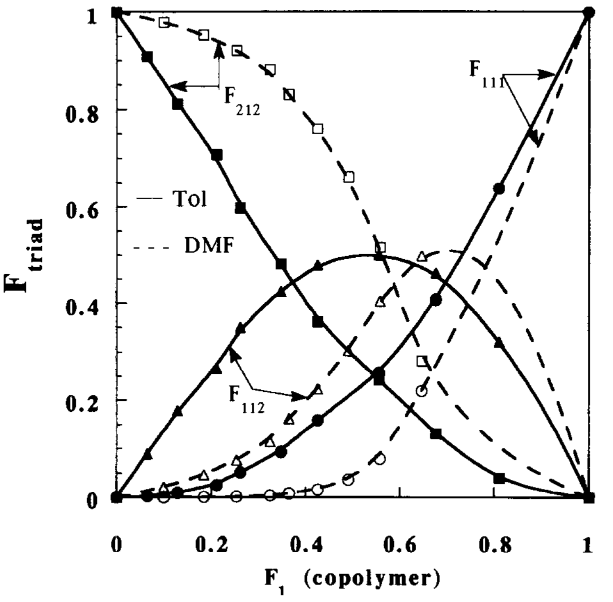

Figure 5 The molar fraction of NVC centred triads vs molar fraction of NVC in the copolymer (F_1)

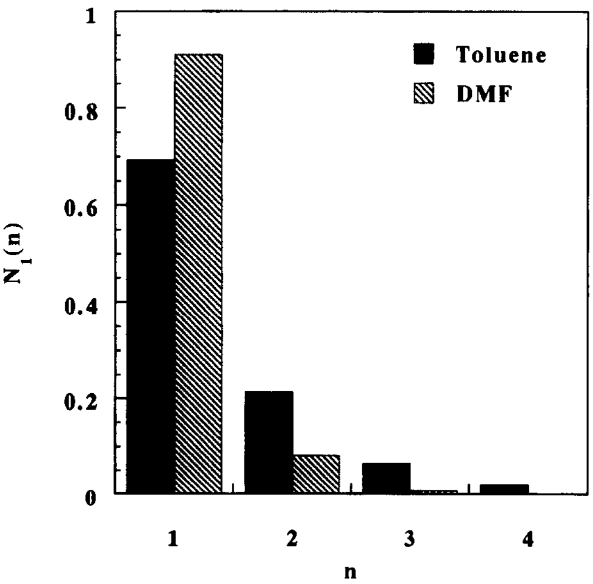

Figure 6 Number fraction N_1 (n) of NVC sequences with length n, as a function of n, for copolymers prepared from a monomer feed ratio of 50/50 in toluene and DMF

However, copolymers prepared from a monomer feed of $f_1 = 0.50$ but in different solvents, having about the same composition, showed different microstructure (*Figure 4*). In *Figure 4* the molar fraction of NVC centred triads was plotted as a function of NVC in the monomer feed; the molar fractions were calculated from the determined reactivity ratios, taking into account the equations given in the literature[18]. It is observed that the copolymer from a monomer feed of $f_1 = 0.50$ prepared in DMF appear a much higher molar fraction of alternating triads $m_1m_2m_1$ and lower fraction of triads $m_1m_1m_1$ and $m_1m_1m_2$ than the corresponding copolymer prepared in toluene.

The solvent effect on the microstructure of the copolymer is also shown in *Figure 5*, where the molar fraction of NVC centred triads was plotted as a function of NVC in the copolymer. It is clear now that copolymers with the same composition obtained in different solvents have different microstructure. It is noteworthy that in systems which follow the bootstrap model, copolymers obtained in different solvents from the same monomer feed have different microstructure, but copolymers of the same composition have the same microstructure[2,3,14].

The difference in the microstructure of copolymers with about the same composition ($F_1 = 0.348$ and $F_1 = 0.365$) prepared from a monomer feed of $f_1 = 0.50$ in toluene and DMF is more clearly shown in *Figure 6*, which illustrates by means of a bar graph how the number fraction of NVC sequences with length n varies with n. In copolymer prepared in toluene about 69% of the NVC units are sandwiched between two DMAEMA units while in copolymer from DMF this fraction is increased to about 91%, indicating the higher tendency of comonomers towards alternation.

Finally it is noteworthy that not only does the copolymerization solvent effect the composition and microstructure of copolymers, but obviously so do their molecular weight through chain transfer reactions with the propagating macroradicals. The larger the chain transfer constant of solvent to comonomers, the lower the molecular weight of the copolymer. Generally the polar solvents show larger chain transfer constants to various monomers than the non-polar solvents. So copolymers prepared in the polar DMF should have lower molecular weights than the corresponding ones prepared in the non-polar toluene.

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