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Bulk copolymerization of methacrylonitrile with n-alkyl methacrylates: rate of copolymerization and reactivity ratios

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The bulk copolymerization of methacrylonitrile with methyl, ethyl and butyl methacrylates, initiated by AIBN under high vacuum, was studied dilatometrically at 60°C. The composition of the reaction medium sensitively affects the overall rate of copolymerization in such a way that a decrease in the copolymerization rate with increasing concentration of methacrylonitrile in the feed was observed. The reactivity ratios of the three systems were calculated according to the general copolymerization equation, from composition data of copolymer samples determined by ^{1}H n.m.r. spectroscopy. The values obtained indicate that the methacrylonitrile/methyl methacrylate system approaches ideal behaviour and the other two systems seem to fit a typical random copolymerization.

(Keywords: methacrylonitrile; methacrylates; dilatometry; reactivity ratios)

INTRODUCTION

The synthesis and properties of copolymers based on the reaction of acrylates or methacrylates with nitrogen-containing monomers can be found in the literature[1–4]. The aim of this study was to improve some properties, mainly the thermal stability, of acrylate and methacrylate polymers.

In this paper the process of free radical copolymerization of several methacrylates with n-alkyl side chains with methacrylonitrile is described. The overall copolymerization rate for different compositions of the monomer feed was obtained dilatometrically. Although the reactivity ratios of the comonomers were reported by Cameron *et al.* in 1959[5] using nitrogen analysis to determine the methacrylonitrile content in the copolymers, in this paper the reactivity ratios are calculated from copolymer composition data by using the Fineman–Ross[6] and Kelen–Tudos[7] methods and by the application of the non-linear least square analysis of Tidwell and Mortimer[8] which provides a unique value for these parameters.

EXPERIMENTAL

Reagents: Methacrylonitrile (N), methyl methacrylate (M), ethyl methacrylate (E) and n-butyl methacrylate (B) (Merck) were purified by washing three times with 5% NaOH aqueous solution and then several times with distilled water. After separation and drying over calcium chloride, the monomers were distilled and stored at low temperature. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized twice from ethanol (m.p. = 104°C).

Polymerization: The bulk copolymerization reactions for the three N/M, N/E and N/B systems were followed dilatometrically at 60 ± 0.5°C. The dilatometers, previously calibrated, containing the required amount of monomer and initiator ([AIBN] = 5×10^{-3} mol l^{-1}) were degassed as many times as necessary to obtain no evacuation by the usual freezing-thawing cycles under

Table 1 Values of volume change of alkyl methacrylates and methacrylonitrile

Monomer	Density (g cm^{-3}) at 60°C		Volume change (%)
	Monomer	Polymer	
Methyl methacrylate	0.897[a]	1.191[a]	24.7
Ethyl methacrylate	–	–	24.0[d]
Butyl methacrylate	0.857[b]	1.030[c]	16.8
Methacrylonitrile	–	–	34.7[e]

[a] Ref. 9
[b] Experimental
[c] Ref. 11
[d] Ref. 10
[e] Ref. 12

Table 2 Experimental data for the copolymerization of methacrylonitrile with methyl methacrylate at 60 ± 1°C initiated by AIBN

F_M[a]	f_M[a]	Reaction time (min)	Conversion (%)	Copolymerization rate (mol l^{-1} s^{-1})
0.200	0.20_9	171	1.57	1.48
0.400	0.40_5	126	1.14	1.96
0.500	0.51_0	81	1.12	2.09
0.600	0.59_0	78	1.25	2.87
0.800	0.79_1	96	2.40	4.11
0.900	0.89_0	55	1.25	7.32

[a] F_M and f_M are the molar fraction of methyl methacrylate in the feed and in the copolymer, respectively

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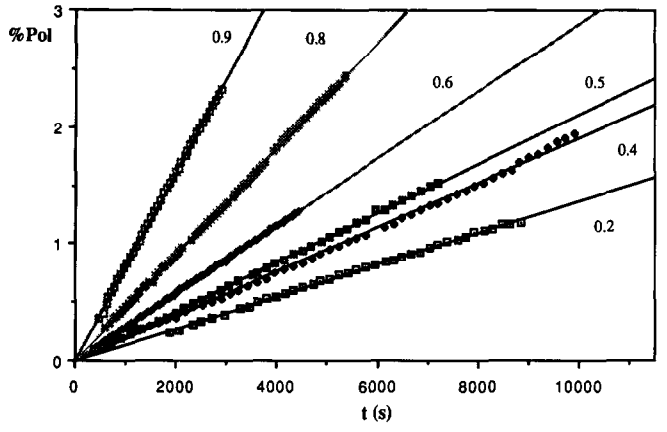

Figure 1 Conversion (wt%) *versus* time for the free radical copolymerization of methacrylonitrile with methyl methacrylate at 60°C. The values for the molar fraction of methyl methacrylate in the feed are shown

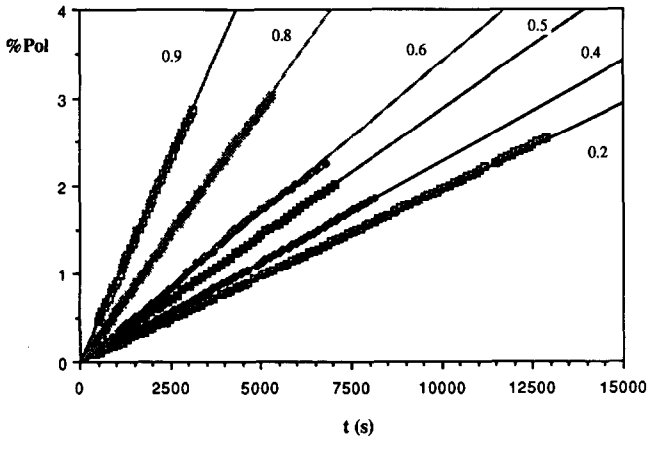

Figure 2 Conversion (wt%) *versus* time for the free radical copolymerization of methacrylonitrile with ethyl methacrylate at 60°C. The values for the molar fraction of ethyl methacrylate in the feed are shown

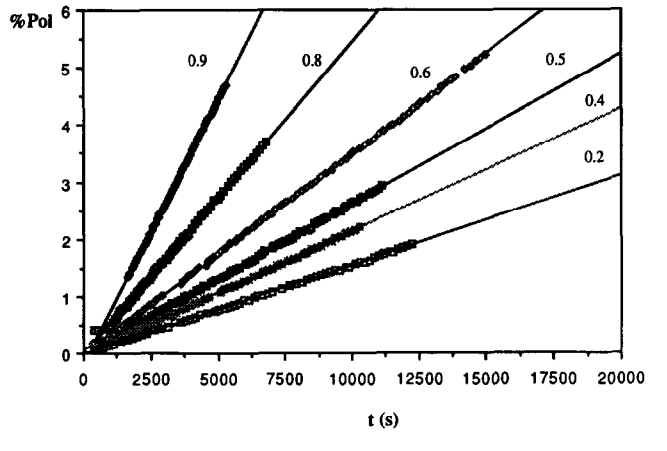

Figure 3 Conversion (wt%) *versus* time for the free radical copolymerization of methacrylonitrile with butyl methacrylate at 60°C. The values for the molar fraction of butyl methacrylate in the feed are shown

high vacuum ($>10^{-4}$ mm Hg) and then sealed. The amount of time for copolymerization to take place was obtained experimentally and was short enough for the conversion of monomers below 5 wt% (0.9–4.3 h). After this time, the dilatometers were immersed in liquid nitrogen. The samples were diluted with dimethyl formamide (DMF) and poured into a large excess of cool methanol. The precipitated products were purified by dissolving the isolated samples in DMF and precipitating in excess methanol. Finally, they were dried to constant weight under vacuum at 40°C.

Copolymer composition: The composition of the copolymer samples was determined by ^{1}H n.m.r. spectroscopy. The spectra were recorded at 80°C on 20% (w/v) perdeuterated dimethylsulphoxide (DMSO-d_6), by means of a Varian VXR-300 spectrometer.

RESULTS AND DISCUSSION

Dilatometry

As is well known, dilatometry uses the volume change that occurs upon polymerization to follow the conversion–time relationship. It is often the most accurate method for chain polymerization reactions because of the large difference in density between monomer and polymer. *Table 1* shows the values of the density (monomers and polymers) and/or volume change (%) for the polymerization of methacrylonitrile and the alkyl methacrylates used in this work.

Table 3 Experimental data for the copolymerization of methacrylonitrile with ethyl methacrylate at 60 ± 1°C initiated by AIBN

F_E[a]	f_E[a]	Reaction time (min)	Conversion (%)	Copolymerization rate (mol l^{-1} s^{-1})
0.201	0.31_2	218	2.02	2.13
0.420	0.51_6	200	2.08	2.14
0.567	0.61_1	120	1.09	2.32
0.632	0.68_9	116	2.04	2.49
0.825	0.84_2	93	2.33	4.68
0.904	0.90_6	58	2.60	7.39

[a] F_E and f_E are the molar fraction of ethyl methacrylate in the feed and in the copolymer, respectively

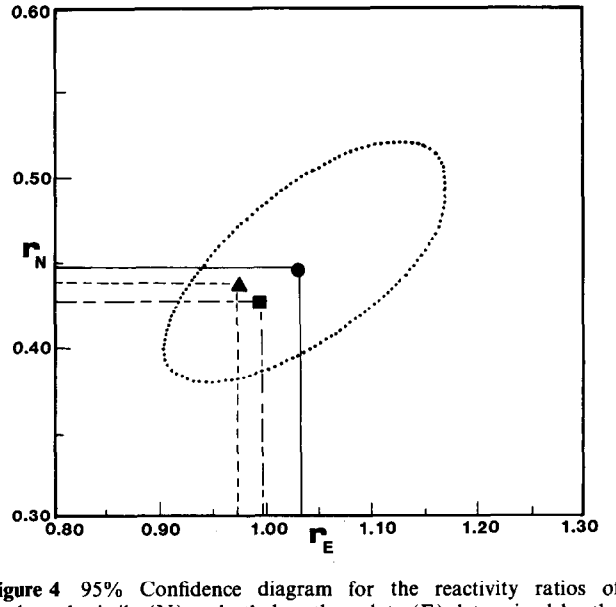

Figure 4 95% Confidence diagram for the reactivity ratios of methacrylonitrile (N) and ethyl methacrylate (E) determined by the non-linear least square method suggested by Tidwell and Mortimer. Values of reactivity ratios: (●) Tidwell–Mortimer; (■) Kelen–Tudos; (▲) Fineman–Ross

Table 4 Experimental data for the copolymerization of methacrylonitrile with butyl methacrylate at 60 ± 1°C initiated by AIBN

F_B[a]	f_B[a]	Reaction time (min)	Conversion (%)	Copolymerization rate (mol l^{-1} s^{-1})
0.186	0.30_5	205	1.80	1.47
0.348	0.46_4	177	3.76	1.86
0.452	0.56_5	189	2.80	2.14
0 582	0.68_0	255	4.80	2.63
0.785	0.81_1	121	2.16	3.67
0.902	0.91_6	90	3.70	5.80

[a] F_B and f_B are the molar fraction of butyl methacrylate in the feed and in the copolymer, respectively

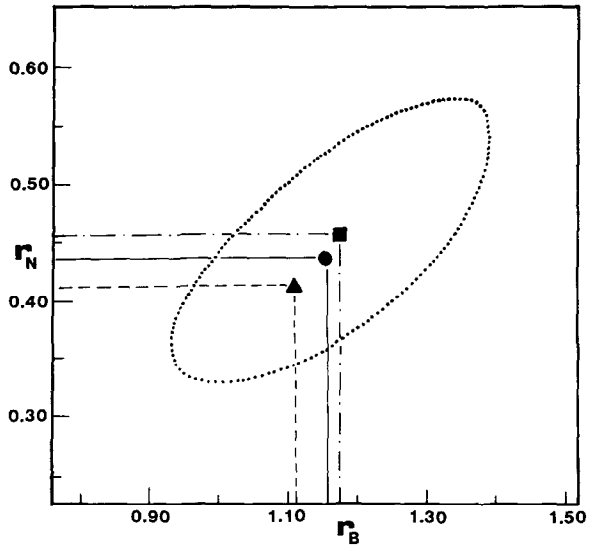

Figure 5 95% Confidence diagram for the reactivity ratios of methacrylonitrile (N) and butyl methacrylate (B) determined by the non-linear least square method suggested by Tidwell and Mortimer. Values of reactivity ratios: (●) Tidwell–Mortimer; (■) Kelen–Tudos; (▲) Fineman–Ross

The copolymerization of N with M, E and B initiated by AIBN have been studied over a wide composition range, with molar fractions of the corresponding methacrylates between 0.2 and 0.9 in the monomer feed. Plots of percentage polymer *versus* time for the three copolymer systems afforded good linearity. Examples are shown in *Figures 1–3*. The rates of copolymerization were obtained from the slopes of the straight lines taking into account the overall monomer concentration in the feed. *Tables 2–4* give information on the copolymerization reactions for the three systems studied. The rate of copolymerization of N with methacrylates is a function of the concentration of the monomers. As is shown in *Tables 2–4*, the overall rate of copolymerization increases with increasing methacrylate molar fraction in the feed. However, this parameter does not depend on the size of the alkyl group in the methacrylates. Taking into account the radical homopolymerization of methacrylates found in the literature[13–15], the rate of polymerization increases with the increasing length of the n-alkyl side group, but this behaviour is not observed even when small amounts of N are present. Hence, it seems reasonable to assume that some interactions between N and the corresponding methacrylate can occur during copolymerization. These interactions could involve both nitrile and carbonyl groups of the monomers and growing radicals[16].

Reactivity ratios

The reactivity ratios r_1 and r_2 for the three systems studied were calculated by using the Fineman–Ross[6] and Kelen–Tudos[7] linearization methods as well as by the application of the non-linear least square analysis suggested by Tidwell and Mortimer[8].

Non-linear least square analysis allows the desired parameters to be determined and the precision of the method to be obtained. Thus, the application of the mathematical treatment suggested by Behnken[17] and Tidwell and Mortimer[8] provides the so-called 95% confidence limit which gives an idea of the experimental error and of the goodness of the experimental conditions

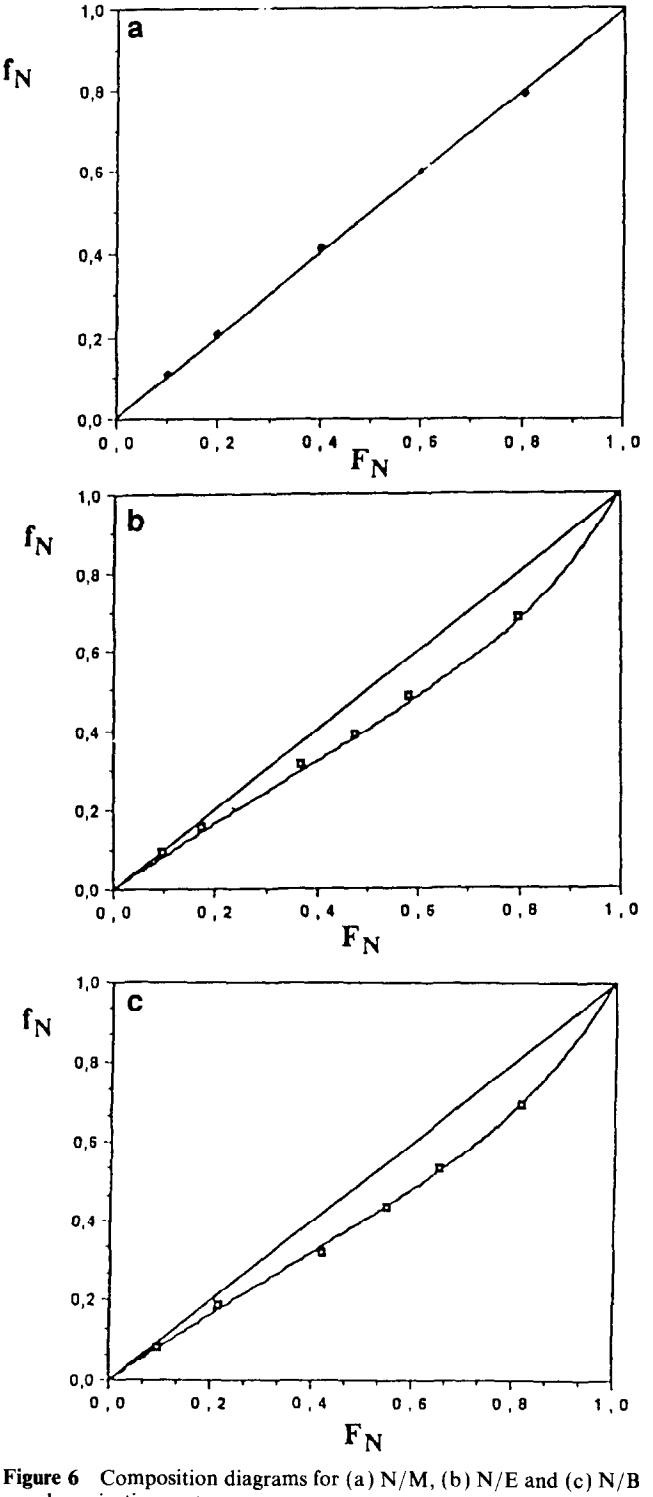

Figure 6 Composition diagrams for (a) N/M, (b) N/E and (c) N/B copolymerization systems

Table 5 Reactivity ratios of alkyl methacrylates (M, E and B) with methacrylonitrile (N)

System	r	Fineman–Ross method	Kelen–Tudos method	Tidwell–Mortimer method	Ref. 5
M/N	r_M	0.905 ± 0.020	0.905 ± 0.020	0.892	0.74
	r_N	0.908 ± 0.030	0.892 ± 0.020	0.883	0.70
	$r_M r_N$	0.822	0.805	0.788	0.52
E/N	r_E	0.976 ± 0.020	0.994 ± 0.020	1.030	0.83
	r_N	0.439 ± 0.030	0.428 ± 0.020	0.445	0.46
	$r_E r_N$	0.428	0.425	0.458	0.38
B/N	r_B	1.172 ± 0.020	1.111 ± 0.020	1.156	0.69
	r_N	0.453 ± 0.030	0.411 ± 0.020	0.432	0.51
	$r_B r_N$	0.531	0.457	0.499	0.35

used to calculate the composition data. This limit is defined by the area of the elliptical diagram drawn in *Figures 4* and *5*. The corresponding diagram obtained from the N/M pair has been reported in a previous paper[16]. These diagrams confirm the good approximation of the values of r_1 and r_2 as indicated by the reduced dimensions of the ellipses, and thus the values of the reactivity ratios obtained by the non-linear least square analysis are the most appropriate values to be used.

The values of r_1 and r_2 determined by the three methods are quoted in *Table 5*. The application of these results to the Lewis–Mayo equation gives copolymer compositions very close to the measured values as is shown in *Figure 6*, where the experimental points fit the corresponding composition diagrams calculated from reactivity ratios determined by the Tidwell–Mortimer method for all the copolymerization systems. According to these results, as can be observed in *Table 5*, the product of r_1 and r_2 is nearly unity for the M/N system, indicating that the copolymerization of N with M approaches ideal behaviour, with a random monomer distribution, and for the other two systems it remains less than unity, indicating that in both cases the copolymers are weakly ordered, with a predominantly random distribution of monomeric units in the polymer chains, although there is a relative tendency towards the alternation of monomeric units specially for low N concentrations.

The relative reactivities of growing chains ending in N radicals for the N/M, N/E and N/B pairs are 1.13, 2.25 and 2.31, respectively. Thus, for the N/M system, these radicals present rather similar reactivity towards M and N monomer molecules, whereas for the N/E and N/B systems, the radicals ending in N are more reactive towards E or B than towards its own monomer. With respect to the reactivity of the growing chains ending in methacrylate units, these radicals present a rather similar tendency to react either with its own monomer or with N.

On establishing a relationship between the kinetic data and the reactivity ratios data, it can be observed that the similar decrease in the overall rate of copolymerization as the N concentration increases in the feed for all the systems is not consistent with the different values of N reactivity (r_1) in each copolymerization. This reaffirms the hypothesis that the rate of copolymerization may depend on some interaction between both monomers. In this sense, this interaction should be reflected in the microstructure of these copolymers, as has been verified by the structural analysis of N/M copolymers reported elsewhere[16].

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