

Solution Copolymerization of Alkyl Methacrylates and *N*-Vinyl Carbazole: Reactivity Ratios

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SYNOPSIS

The copolymerization of ethyl methacrylate and *n*-butyl methacrylate with *N*-vinyl carbazole was studied at 60°C, using AIBN as the initiator. The reactivity ratios of the monomers were determined in benzene, ethyl acetate, acetone or (*N,N*-dimethylformamide) solutions. The values of r_1 and r_2 were calculated by the Fineman–Ross and Kelen–Tüdös methods and were compared with those obtained earlier in bulk copolymerization.

INTRODUCTION

The bulk and solution copolymerization of *N*-vinyl carbazole with vinyl monomers, such as methyl acrylate, methyl methacrylate, or styrene, has been studied by several authors.^{1–6} The results of the investigations of the radical copolymerization of ethyl and *n*-butyl methacrylates with *N*-vinyl carbazole were presented previously.⁷ The reactivity ratios of the comonomers have been determined in bulk, but only for six compositions because of the poor solubility of *N*-vinyl carbazole in the methacrylates.

As is well known, the polymerization medium often greatly affects the reactivity of monomers. Therefore, this work deals with the radical copolymerization of the same monomers in different solvents. The relation between the reactivity ratios and the solubility parameters (δ) of the solvents is discussed. The reactivity ratios, r_1 and r_2 , of the comonomers have been calculated using the methods of Fineman–Ross⁸ and Kelen–Tüdös.^{9–11}

EXPERIMENTAL

Monomers

N-vinyl Carbazole (*N*-VC), Pure (Fluka A.G., Switzerland)

The monomer was purified by two-fold recrystallization from heptane and methanol. The melting

point (mp) was from 63.5–65.0°C. The content of nitrogen, determined by Kjeldahl's method,¹² was 13.49% (calculated 13.51).

Ethyl Methacrylate (EMA), Pure (Fluka A.G. Switzerland)

The monomer was separated from the initiator as in Ref. 13 and was dried over anhydrous magnesium sulphate. It was distilled under reduced pressure just before use. $n_D^{20} = 1.4140$; $d_4^{20} = 0.9110$ g/cm³.

n-Butyl Methacrylate (*n*-BMA), Pure (Oświęcim Chemical Plant, Poland)

The monomer was purified in the same manner as ethyl methacrylate. $n_D^{20} = 1.4210$; $d_4^{20} = 0.8940$ g/cm³.

α, α' -Azobisisobutyronitrile (AIBN), Pure (BDH Chemicals Ltd., England)

Reagent grade AIBN was dissolved in chloroform. The solution was filtered and the solute was precipitated with diethyl ether. The procedure was repeated twice. The mp was 102°C.

The solvents benzene, ethyl acetate, acetone, *N,N*-dimethylformamide, or methanol were all analytical grade reagents. They were purified using standard methods and were distilled just before used.

Copolymerization Procedure

The copolymerizations were carried out in a solvent in sealed glass ampules (10 ± 2 mL) at $60^\circ\text{C} \pm 1^\circ\text{C}$ with AIBN as initiator. The time of copolymeriza-

Table I Experimental Data for the Copolymerization of Ethyl Methacrylate (M_1) with N -Vinyl Carbazole (M_2) at 60°C in the Presence of AIBN (0.3% by wt) in Benzene

Composition of Starting Mixture (mol %)		Polymerization Time (h)	Conversion (wt%)	N Content in Copolymer (wt%)	Fraction of N -VC in Copolymer (mol %)	Mean Sequence Length	
M_1	M_2					μ_1	μ_2
90	10	2.00	1.60	0.40	3.34	94.10	1.00
80	20	1.83	2.90	0.75	6.38	48.12	1.00
70	30	1.66	2.60	1.25	10.96	26.10	1.01
60	40	1.50	4.20	1.55	13.84	20.10	1.01
50	50	1.33	6.30	2.00	18.37	15.28	1.01
40	60	1.17	9.70	2.50	23.71	11.34	1.02
30	70	1.00	5.93	3.05	30.00	8.49	1.02
20	80	0.83	7.77	3.75	38.73	6.08	1.03
10	90	0.67	9.90	4.75	52.82	3.87	1.06

Total monomer concentration: 1.96 mol/L.

tion was established experimentally. The time was short enough to obtain conversions below 10%. Only for the system of EMA— N -VC in benzene was the conversion about 30%. After copolymerization, the ampules were taken from the thermostat, cooled down quickly to room temperature, and broken into acetone. The copolymer was isolated and purified by two precipitation-dissolving cycles in acetone and methanol. The copolymer was then filtered off and dried *in vacuo* at room temperature to constant weight.

Copolymer Analysis

The copolymer compositions were calculated from nitrogen contents determined by Kjeldahl's method. Each copolymer was analyzed for nitrogen three times. The results were reproducible within 0.2–0.3%. For each pair of comonomers, two series of measurements for nine compositions were made. The average results for two series of copolymerization experiments for EMA— N -VC and n -BMA— N -VC in various solvents are shown in Ta-

Table II Experimental Data for the Copolymerization of Ethyl Methacrylate (M_1) with N -Vinyl Carbazole (M_2) at 60°C in the Presence of AIBN (0.3% by wt) in Benzene (High Conversion)

Composition of Starting Mixture (mol %)		Polymerization Time (h)	Conversion (wt%)	N Content in Copolymer (wt%)	Fraction of N -VC in Copolymer (mol %)	Mean Sequence Length	
M_1	M_2					μ_1	μ_2
90	10	4.25	24.40	0.45	3.76	71.59	1.01
80	20	3.83	27.40	0.95	8.18	31.98	1.02
70	30	3.67	27.70	1.45	12.87	19.69	1.03
60	40	3.50	28.10	2.00	18.37	13.27	1.04
50	50	3.33	28.40	2.50	23.71	9.88	1.06
40	60	1.42	31.00	3.10	30.60	7.26	1.09
30	70	1.33	31.20	3.80	39.40	5.25	1.13
20	80	1.17	30.50	4.60	50.57	3.70	1.20
10	90	1.00	30.40	5.80	70.15	2.17	1.46

Total monomer concentration: 1.92 mol/L.

Table III Experimental Data for the Copolymerization of Ethyl Methacrylate (M_1) with *N*-Vinyl Carbazole (M_2) at 60°C in the Presence of AIBN (0.3% by wt) in Ethyl Acetate

Composition of Starting Mixture (mol %)		Polymerization Time (h)	Conversion (wt%)	<i>N</i> Content in Copolymer (wt%)	Fraction of <i>N</i> -VC in Copolymer (mol %)	Mean Sequence Length	
M_1	M_2					μ_1	μ_2
90	10	2.00	4.69	0.40	3.34	91.00	1.01
80	20	1.75	3.97	0.80	6.83	43.33	1.01
70	30	1.50	5.59	1.40	12.39	22.97	1.03
60	40	1.25	5.49	1.80	16.32	16.46	1.04
50	50	1.00	4.60	2.45	23.16	11.30	1.05
40	60	0.90	4.52	3.00	29.41	8.45	1.07
30	70	0.77	3.56	3.60	36.79	6.33	1.10
20	80	0.63	6.37	4.50	49.10	4.22	1.17
10	90	0.50	7.47	5.50	64.90	2.68	1.33

Total monomer concentration: 1.96 mol/L.

bles I-VI. The IR spectra (KBr pellets) were recorded on a SPECORD-71 IR spectrometer (Carl Zeiss Jena, Germany).

RESULTS AND DISCUSSION

The radical copolymerization of EMA and *N*-VC with AIBN as initiator was investigated in selected solvents of different dipole moments (μ). The copolymerization of *n*-BMA with *N*-VC was carried

out in benzene only. The experimental results for the system of EMA-*N*-VC are listed in Tables I-II (benzene, low and high conversions), Table III (ethyl acetate), Table IV (acetone), and Table V (*N,N*-dimethylformamide). The results for the *n*-BMA-*N*-VC system in benzene are presented in Table VI. The structure of the copolymers was verified using infrared spectra. Figure 1 shows IR spectra for poly(*N*-VC) (I), and for copolymers of EMA-*N*-VC obtained in bulk (II), and in two solvents: ethyl acetate (III) and *N,N*-dimethylform-

Table IV Experimental Data for the Copolymerization of Ethyl Methacrylate (M_1) with *N*-Vinyl Carbazole (M_2) at 60°C in the Presence of AIBN (0.3% by wt) in Acetone

Composition of Starting Mixture (mol %)		Polymerization Time (h)	Conversion (wt%)	<i>N</i> Content in Copolymer (wt%)	Fraction of <i>N</i> -VC in Copolymer (mol %)	Mean Sequence Length	
M_1	M_2					μ_1	μ_2
90	10	2.00	4.62	0.45	3.76	71.76	1.00
80	20	1.75	5.44	0.90	7.74	33.94	1.01
70	30	1.50	6.89	1.40	12.39	20.55	1.01
60	40	1.25	5.24	1.90	17.34	14.17	1.02
50	50	1.00	6.54	2.40	23.16	10.17	1.03
40	60	0.90	6.66	3.00	29.41	7.63	1.04
30	70	0.77	5.08	3.60	36.79	5.75	1.05
20	80	0.63	6.13	4.25	45.51	4.31	1.10
10	90	0.50	6.86	5.00	56.69	3.11	1.12

Total monomer concentration: 1.96 mol/L.

Table V Experimental Data for the Copolymerization of Ethyl Methacrylate (M_1) with *N*-Vinyl Carbazole (M_2) at 60°C in the Presence of AIBN (0.3% by wt) in DMF

Composition of Starting Mixture (mol %)		Polymerization Time (h)	Conversion (wt%)	<i>N</i> Content in Copolymer (wt%)	Fraction of <i>N</i> -VC in Copolymer (mol %)	Mean Sequence Length	
M_1	M_2					μ_1	μ_2
90	10	1.83	9.85	0.30	2.49	156.311	1.01
80	20	1.58	9.51	0.70	5.94	63.74	1.01
70	30	1.42	9.90	1.10	9.56	38.49	1.02
60	40	1.17	9.79	1.60	14.33	24.68	1.03
50	50	1.00	9.01	2.15	19.93	16.93	1.04
40	60	0.90	9.73	2.80	27.08	11.66	1.10
30	70	0.77	9.86	3.50	35.52	8.19	1.10
20	80	0.63	9.76	4.30	46.22	5.61	1.15
10	90	0.50	9.19	5.15	59.08	3.74	1.26

Total monomer concentration: 1.96 mol/L.

amide (IV). IR spectra for the copolymers (I, II, III) were almost identical. The characteristic bands for *N*-VC are at 3010 cm^{-1} , at 1610–1595 cm^{-1} , and 1485 cm^{-1} (aromatic), as well as for methacrylates below 3000 cm^{-1} (aliphatic) and at 1730 cm^{-1} and 1145 cm^{-1} (esters). As shown in Tables I–VI, the rate of polymerization of methacrylates with *N*-VC is a function of the concentration of comonomers. For both systems, EMA–*N*-VC and *n*-BMA–*N*-VC, the rate of polymerization increased with increasing content of *N*-VC in the feed. The rates of polymerization in solvents, such as benzene (low

conversions), ethyl acetate, and acetone, were similar. Somewhat higher rates of polymerization were observed for the system EMA–*N*-VC in DMF and in benzene at high conversions.

The monomer reactivity ratios of methacrylates r_1 and *N*-VC r_2 have been determined according to the Fineman–Ross⁸ (F–R) and Kelen–Tüdös^{9–11} (K–T) procedures. In the latter, two methods of calculations were used: graphical methods with weight conversion taken into account¹⁰ (I), and the least square method¹¹ (II). The results are presented in Table VII. Figures 2 and 3 show examples of the

Table VI Experimental Data for the Copolymerization of *n*-Butyl Methacrylate (M_1) with *N*-Vinyl Carbazole (M_2) at 60°C in the Presence of AIBN (0.3% by wt) in Benzene

Composition of Starting Mixture (mol %)		Polymerization Time (h)	Conversion (wt%)	<i>N</i> Content in Copolymer (wt%)	Fraction of <i>N</i> -VC in Copolymer (mol %)	Mean Sequence Length	
M_1	M_2					μ_1	μ_2
90	10	2.00	4.06	0.45	4.62	51.94	1.04
80	20	1.75	3.22	0.90	9.40	24.79	1.08
70	30	1.50	2.28	1.50	16.03	13.83	1.14
60	40	1.25	4.25	1.15	23.56	9.01	1.23
50	50	1.00	3.17	2.85	32.12	6.22	1.35
40	60	0.90	3.04	3.65	49.45	3.52	1.72
30	70	0.77	3.20	4.55	55.07	3.01	1.90
20	80	0.63	3.90	5.50	69.44	2.09	2.67
10	90	0.50	4.63	6.50	85.10	1.40	5.50

Total monomer concentration: 1.79 mol/L.

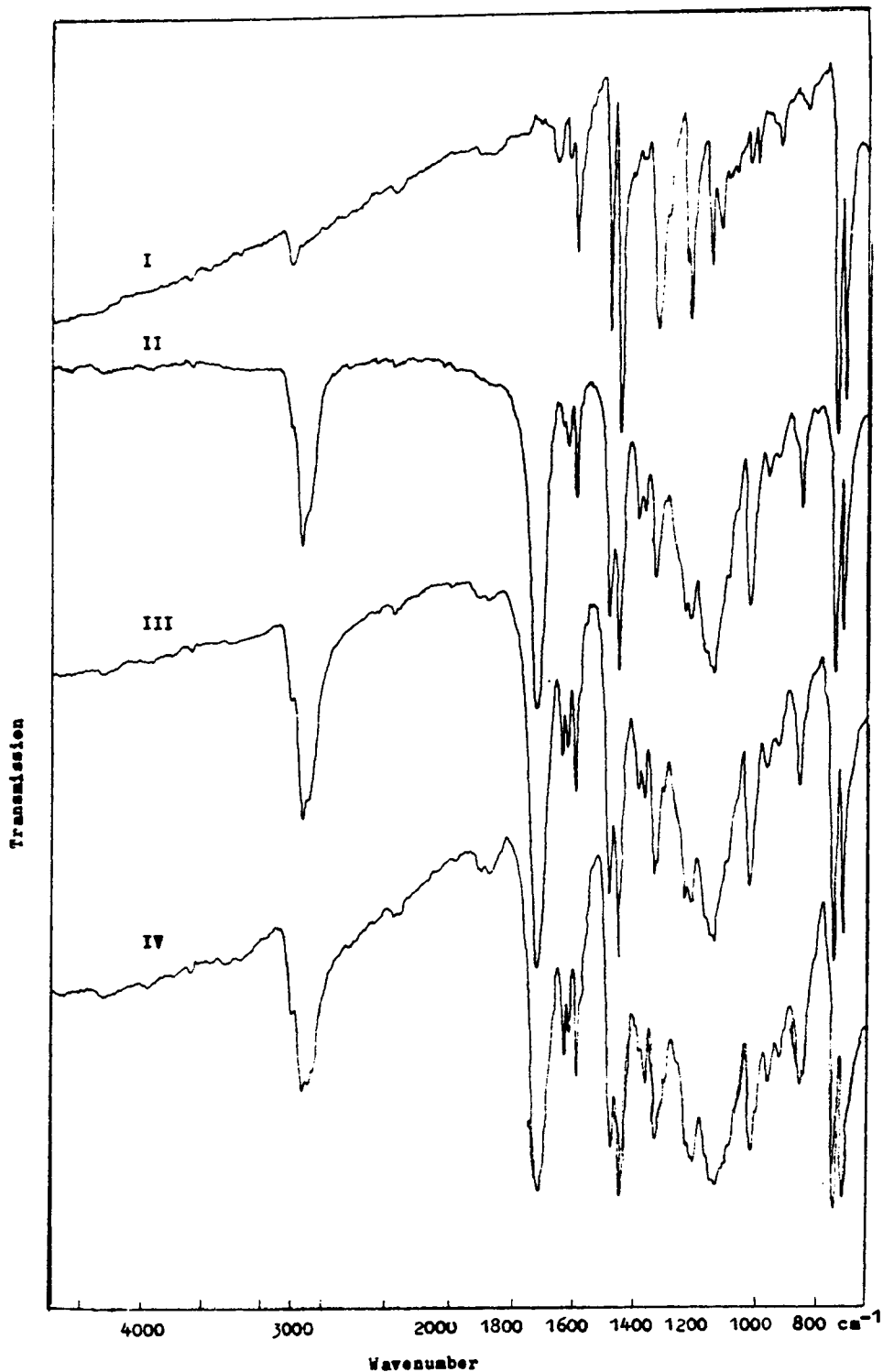


Figure 1 IR spectra of poly(*N*-VC) (I), and copolymers of EMA—*N*-VC, (II) in bulk (50 mol % of *N*-VC), (III) in ethyl acetate (50 mol % of *N*-VC), and (IV) in DMF (40 mol % of *N*-VC).

K-T plots for EMA—*N*-VC and *n*-BMA—*N*-VC systems in benzene. As can be seen in Table VII, all methods of calculations yielded similar results. It is

interesting to note that the reactivity ratios for EMA—*N*-VC, determined in benzene at high conversion steps, are different from those determined

Table VII Reactivity Ratios of Alkyl Methacrylates (r_1) with *N*-Vinyl Carbazole (r_2) in Various Solvents

Solvent	μ^a	δ^b	r	Fineman-Ross Method	Kelen-Tüdös method	
					I	II
EMA—N-VC System						
Benzene	0	18.8	r_1	3.15	3.210	3.212
Benzene	0	18.8	r_2	0.050	0.050	0.050
Benzene	0	18.8	$r_1 r_2$	0.157	0.161	0.173
Benzene	0	18.8		2.78	2.756	2.760
Benzene	0	18.8	r_2^c	0.213	0.197	0.197
Benzene	0	18.8	$r_1 r_2^c$	0.592	0.543	0.544
Ethyl acetate	1.78	18.6	r_1	3.19	3.136	3.105
Ethyl acetate	1.78	18.6	r_2	0.206	0.151	0.177
Ethyl acetate	1.78	18.6	$r_1 r_2$	0.656	0.474	0.549
Acetone	2.71	20.3	r_1	2.77	2.790	2.763
Acetone	2.71	20.3	r_2	0.110	0.081	0.092
Acetone	2.71	20.3	$r_1 r_2$	0.305	0.226	0.254
DMF	3.82	24.8	r_1	4.30	3.999	3.961
DMF	3.82	24.8	r_2	0.292	0.158	0.171
DMF	3.82	24.8	$r_1 r_2$	1.255	0.632	0.701
<i>n</i>-BMA—NVC System						
Benzene	0	18.8	r_1	2.39	2.481	2.468
Benzene	0	18.8	r_2	0.672	0.715	0.734
Benzene	0	18.8	$r_1 r_2$	1.603	1.603	1.812
Bulk Copolymerization ^d			r_1	5.67	5.689	5.680
Bulk Copolymerization ^d			r_2	0.020	0.023	0.680
Bulk Copolymerization ^d			$r_1 r_2$	0.113	0.131	0.130

^a Dipole moment [D].^b Solvent solubility parameter (δ) [(MPa)^{1/2}].^c Data for high conversion (about 30%).^d Data from Ref. 7.

at low conversions. Thus, it may be inferred that an increase in conversion significantly influences the copolymerization behavior of the monomer pair. The reactivity ratios in both EMA—*N*-VC and *n*-BMA—*N*-VC systems depend on the solvent used. The highest values of r_1 for EMA were obtained in DMF ($r_1 = 3.96$), while the smallest were in acetone ($r_2 = 2.76$). On the other hand, the highest r_2 values were obtained in benzene at high conversions. High r_2 values were also obtained for the *n*-BMA—*N*-VC system (at low conversion). Comparing the r_1 and r_2 values obtained in solvents, we can state that their solubility parameter (δ) exerts some influence on the reactivity ratios. Solubility parameters of DMF ($\delta = 24.8$; $r_1 = 3.96$), of acetone ($\delta = 20.3$; $r_1 = 2.76$), of benzene ($\delta = 18.8$), and of ethyl acetate ($\delta = 18.6$) are almost the same. The reactivity ratios are similar too ($r_1 = 3.112$ and 3.105 , respectively). The r_2 value for *N*-VC is the smallest in benzene.

In the remaining solvents, the r_1 values are different, but the differences are not large. No significant effect of dipole moment of solvents on r_1 and r_2 values was found. In general, the reactivity ratios measured in bulk⁷ were higher than those in solution. Nevertheless, the relative reactivities of comonomers have not changed. Both in bulk and in solution we have $r_1 > 1$; and $r_2 < 1$. This means that both radicals prefer methacrylates and that the copolymers are enriched in methacrylate units. The values of r_1 and r_2 , obtained by applying the K-T method, were used to calculate the μ_1 and μ_2 values.¹⁴ As can be seen in Tables I–VI, the mean sequence length (μ_1 for EMA or *n*-BMA; μ_2 for *N*-VC) changes consistently with the amount of methacrylates or *N*-VC in the feed. Figures 4 and 5 show the calculated relationship of the molar fraction of *N*-VC in the feed (M_2) and the molar fraction in the copolymer (m_2). For both copolymers, the composition curves are similar.

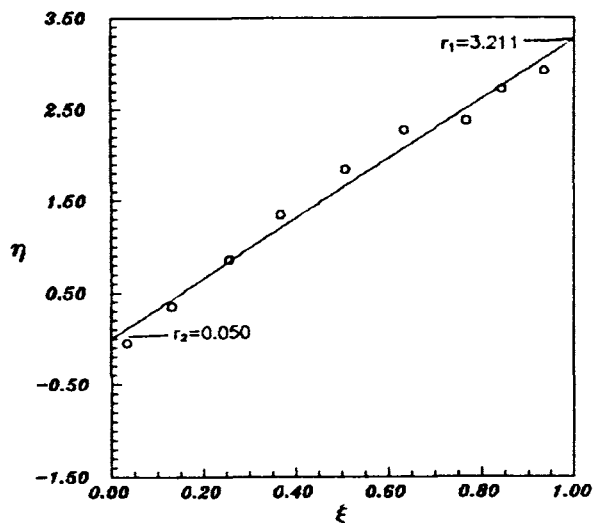


Figure 2 The η vs. ξ for system EMA—*N*-VC in benzene. Kelen-Tüdös method (I); $r_1 = \eta(1)$; $-\frac{r_1}{\alpha} = \eta(0)$, $\alpha = 0.1964$.

The reactivity of methacrylates is high; reactivity causes a rapid change in the composition of the monomer feed. The relatively low conversion of *N*-VC, even at the initial mol fraction of *N*-VC as high as 90%, correlates with low values of r_2 . As can be seen by examining the composition curves and the product of reactivity ratios $r_1 r_2$ (see Table VII), the

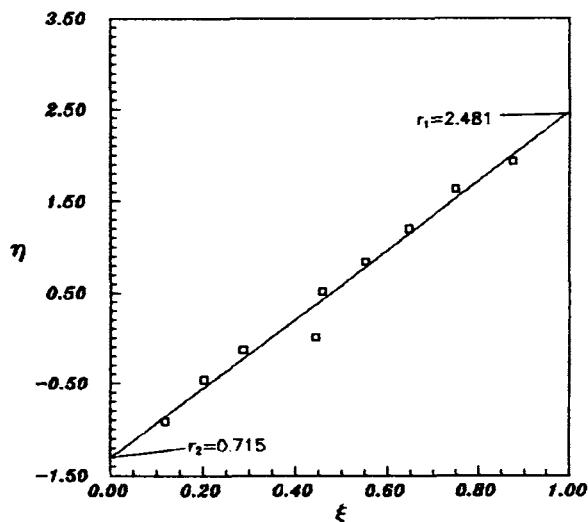


Figure 3 The η vs. ξ plot for system *n*-BMA—*N*-VC in benzene. Kelen-Tüdös method (I); $r_2 = \eta(1)$; $-\frac{r_2}{\alpha} = \eta(0)$, $\alpha = 0.5447$.

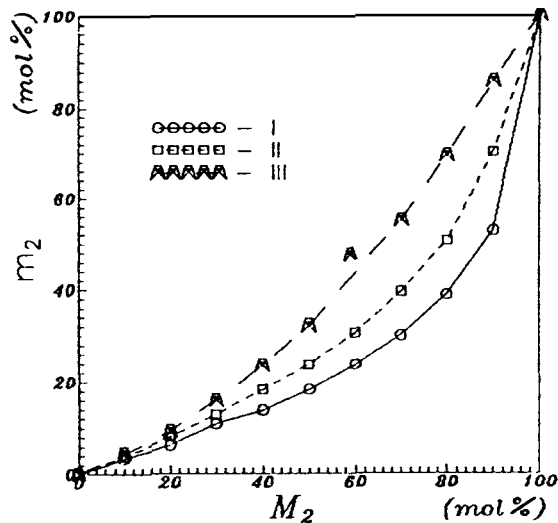


Figure 4 Relationship between the mol fraction of *N*-VC in the feed (M_2) and the mol fraction in the copolymer (m_2) for the systems: (I) EMA—*N*-VC, (II) EMA—*N*-VC at high conversion steps, (III) *n*-BMA—*N*-VC, all in benzene.

copolymers of EMA—*N*-VC formed in all solvents are random. For the system of *n*-BMA—*N*-VC in benzene, the product of reactivity ratios is the highest, $r_1 r_2 = 1.812$. As follows from the composition curve (Fig. 4) and the product of reactivity ratios, the polymerization will proceed with a higher level of *n*-BMA incorporation as compared with EMA.

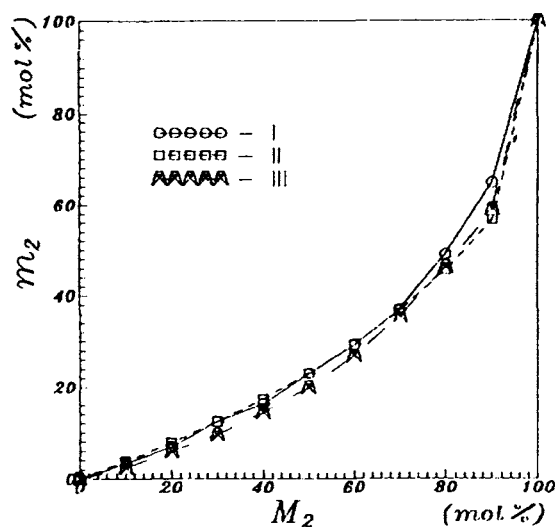


Figure 5 Relationship between the mol fraction of *N*-VC in the feed (M_2) and the mol fraction in the copolymer (m_2) for the systems: (I) EMA—*N*-VC in ethyl acetate, (II) EMA—*N*-VC in acetone, (III) EMA—*N*-VC in DMF.

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