

# Copolymerization of Styrene with *N*-Vinyl Carbazole in Selected Organic Solvents

ANNA RYTTEL

Faculty of Chemistry, Department of Organic Chemistry, Rzeszów Technical University 35-959 Rzeszów, Poland

Received 24 January 1997; accepted 26 April 1997

**ABSTRACT:** The copolymerization of styrene (St) with *N*-vinyl carbazole (*N*-VC) was carried out in different solvents (benzene, ethyl acetate, acetone, or DMF) using  $\alpha, \alpha'$ -azobisisobutyronitrile as an initiator at 60°C. The copolymer compositions were estimated by elemental analysis. The monomer reactivity ratios of styrene ( $r_1$ ) and *N*-VC ( $r_2$ ) were determined by Fineman–Ross and Kelen–Tüdös methods and then recalculated using a nonlinear minimization algorithm based on the Mayo–Lewis method (RREVM). The reactivity ratios calculated by the RREVM method were found to be  $r_1 = 3.74$ ,  $r_2 = 0.14$  (benzene);  $r_1 = 5.02$ ,  $r_2 = 0.11$  (ethyl acetate);  $r_1 = 5.50$ ,  $r_2 = 0.16$  (acetone); and  $r_1 = 5.83$ ,  $r_2 = 0.17$  (DMF). The Alfrey–Price copolymerization parameters  $Q_2$  and  $e_2$  for *N*-VC in each solvent were calculated:  $Q_2 = 0.51$ ,  $e_2 = -1.60$  (benzene);  $Q_2 = 0.37$ ,  $e_2 = -1.57$  (ethyl acetate);  $Q_2 = 0.24$ ,  $e_2 = -1.16$  (acetone); and  $Q_2 = 0.23$ ,  $e_2 = -1.17$  (DMF). © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 715–721, 1998

## INTRODUCTION

The investigations on bulk and solution copolymerization of *N*-vinyl carbazole with vinyl monomers such as styrene and methyl or ethyl methacrylates were carried out by several authors.<sup>1–10</sup> This article reports on our further investigations on the free-radical solution copolymerization of styrene ( $M_1$ ) with *N*-vinyl carbazole ( $M_2$ ) (St–*N*-VC). It is well known that the polymerization medium greatly affects the reactivity ratios. In our earlier studies, the reactivity ratios of ethyl and butyl methacrylates with *N*-VC were determined in the same solvents: benzene, ethyl acetate, acetone, and DMF.<sup>11</sup> In that work, we did not present  $Q$  and  $e$  values for methacrylates, because we could not find reactivity ratios for the system St–*N*-VC in the same solvents (except in benzene).<sup>12</sup> In this article, the reactivity ratios of St ( $r_1$ ) and *N*-VC ( $r_2$ ) were determined in these solvents. The Alfrey–Price<sup>13</sup> copolymerization parameters  $Q_2$  and  $e_2$  for *N*-VC were also calculated.

The aim of this work was on the one hand, the determination of the reactivity ratios of St with *N*-VC in various solvents and evaluation of the values  $Q$  and  $e$  for methacrylates. On the other hand, we tried to relate the reactivity ratios to the solubility parameter ( $\delta$ ) as well as the dipole moment ( $\mu$ ) of the solvents. We also compared the values of the reactivity ratios obtained by different methods. The reactivity ratios were determined by Fineman–Ross<sup>14</sup> and Kelen–Tüdös<sup>15–17</sup> linear methods and recalculated by nonlinear minimization algorithm (RREVM)<sup>18</sup> based on the Mayo–Lewis method.<sup>19</sup> In the Kelen–Tüdös methods, we used the graphical method (I)<sup>15</sup> and the graphical method regarding weight conversion (II).<sup>16–17</sup> Differences of the values of the reactivity ratios obtained by these methods are briefly discussed.

## EXPERIMENTAL

### Monomers

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

The monomer was purified by twofold recrystallization from heptane and methanol. The melting

point (mp) was 63.5–65.0°C. The content of nitrogen, determined by elemental analysis, was 13.49% (calculated 13.51).

**Styrene (St), Pure (International Enzymes Ltd., Windsor, Berkshire, UK)**

The monomer was separated from the initiator as follows: It was twice washed with 5% aqueous sodium bisulfate, then with 8% aqueous sodium hydroxide (also twice), and, at the end, with distilled water to pH 7. The monomer was dried over anhydrous magnesium sulfate and distilled under reduced pressure just before use. The fraction boiling at 37–65.0°C/13–29 mmHg was collected.  $n_D^{20} = 1.5461$ ;  $d_4^{20} = 0.974 \text{ g/cm}^3$ .

**$\alpha, \alpha'$ -Azobisisobutyronitrile (AIBN), Pure (BDH Chemicals Ltd., UK)**

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

**Solvents**

The solvents benzene, ethyl acetate, acetone, DMF, and methanol were all analytical-grade reagents. They were purified using standard methods and were distilled just before use.

**Copolymerization Procedure and Copolymer Analysis**

Free-radical copolymerizations were carried out in sealed glass tubes ( $10 \pm 2 \text{ mL}$ ) at  $60 \pm 1^\circ\text{C}$  with AIBN (0.5% by wt) as the initiator. The appropriate amounts of comonomers at various ratios were weighted and placed with the solvent and initiator into a tube. The total monomer concentration was 2.145 mol/L. The time of copolymerization was established experimentally to reach the conversion of around 10% (ca. 4 h). After that time, the tubes were removed from the bath and cooled to room temperature and the reaction mixture was poured into a large amount of acetone with vigorous stirring. The copolymer was isolated and purified by two precipitation–dissolving cycles in acetone and methanol. The copolymer was further filtered off and dried in a vacuum to a constant weight.

The copolymer compositions were calculated from nitrogen contents determined by elemental analysis of the copolymers, which was performed with an EA1108 elemental analyzer (Carbo Erba,

Italy). Each copolymer was analyzed for nitrogen three times. The results were reproducible within 0.3%. Two series of measurements for nine compositions in each solvent were made.

**RESULTS AND DISCUSSION**

The copolymerization of St ( $M_1$ ) and *N*-VC ( $M_2$ ) with AIBN as the initiator at 60°C was carried out in benzene, ethyl acetate, acetone, and DMF. The average results for two series of copolymerization experiments are shown in Tables I–IV. Although for low polymer concentrations the experimental error of composition determination was relatively high, since the composition of the reaction medium changed with conversion, we had to limit ourselves to low conversion (<10%). The relationship between the rate of copolymerization vs. the mol fraction of *N*-VC in the starting mixture of comonomers in various organic solvents is shown in Figure 1. The experimental results indicate that the rate of copolymerization depends on the concentration of monomers in the starting mixture. The solvents used also significantly affect the copolymerization rate. In general, the rate of copolymerization has a minimum of between a 0.3 and 0.6 mol fraction of *N*-VC in the feed for all solvents.

The monomer reactivity ratios,  $r_1$  for St and  $r_2$  for *N*-VC, were determined according to the Fineman–Ross (F–R)<sup>14</sup> and the Kelen–Tüdös (K–T)<sup>15–17</sup> linear methods and recalculated by a non-linear minimization microcomputer program<sup>18</sup> based on the Mayo–Lewis method.<sup>19</sup> The program employs the Error-in-Variables-Model (RREVM) method to estimate reactivity ratios. In the calculations, the amounts of monomers 1 and 2 (0.3% accuracy) and that of units of the type 2 copolymer (accuracy 3.0%) were introduced as input parameters.

The values of the reactivity ratios calculated by the methods of F–R and K–T and by the RREVM program are summarized in Table V. In the K–T methods, two calculation methods were used: the graphical method<sup>15</sup> (I) and the graphical method with weight conversion taken into account<sup>16–17</sup> (II). Figures 2 and 3 show examples of the K–T plots for the St–*N*-VC system in ethyl acetate and in acetone (graphical methods [I]). In each case for all pairs of comonomers, good straight-line dependencies for terms of the K–T equation were obtained. As can be seen, in Table V, all methods of calculations yielded similar results. However, for the two ways of calculating within the K–T

**Table I** Experimental Data for the Copolymerization of St ( $M_1$ ) with *N*-VC ( $M_2$ ) at 60°C in the Presence of AIBN (0.5% by Wt) in Benzene

Composition of Starting Mixture (mol %)		Polymerization Time (h)	Conversion (Wt %)	Polymerization Rate (Wt %)	N Content in Copolymer (Wt %)	Fraction of <i>N</i> -VC in Copolymer (mol %)	Mean Sequence Length	
$M_1$	$M_2$						$\mu_1$	$\mu_2$
90	10	3.66	3.05	0.83	0.35	2.66	138.33	1.00
80	20	3.58	2.48	0.69	0.77	6.02	59.62	1.01
70	30	3.50	1.91	0.55	1.21	9.75	35.77	1.02
60	40	3.92	1.85	0.47	1.76	14.75	22.73	1.03
50	50	4.00	1.72	0.43	2.31	20.15	15.89	1.04
40	60	4.08	4.27	1.05	2.93	26.80	11.27	1.05
30	70	3.92	6.74	1.74	3.63	35.12	7.94	1.08
20	80	4.00	6.82	1.69	4.34	44.61	5.67	1.11
10	90	4.08	6.95	1.63	5.12	56.50	3.89	1.19

Total monomer concentration: 2.145 mol/L.

method, some differences in resulting  $r_1$  and  $r_2$  values were encountered. The value of  $r_2$  seemed more sensitive toward the calculation method applied.

From the results presented in Table V, it is evident that the reactivity ratios depend on the solvent used. The highest values for both  $r_1$  for St and  $r_2$  for *N*-VC were obtained in DMF ( $r_1 = 5.83$ ;  $r_2 = 0.17$ ) calculated by the RREVM method, the smallest one in benzene ( $r_1 = 3.74$ ;  $r_2 = 0.14$ ). By comparing  $r_1$  and  $r_2$  values (from Table V) in various solvents, one can confirm that their different dipole moment ( $\mu$ ) as well as their solu-

bility parameter ( $\delta$ ) exert a certain influence on the reactivity ratios. No substantial effect of the solubility parameter ( $\delta$ ) on  $r_1$  and  $r_2$  values was found. An interesting dependence of the dipole moment ( $\mu$ ) of the solvents on the reactivity ratios was found. For benzene (dipole moment  $\mu = 0$ ), the value of  $r_1$  is the smallest:  $r_1 = 3.74$ . When the dipole moment of a solvent increases, the value of  $r_1$  becomes higher (for DMF  $\mu = 3.82$ ,  $r_1 = 5.83$ ). The reactivity of St in the copolymerization with *N*-VC is relatively high in all solvents. The value of  $r_1$  is greater than 1, and of  $r_2$ , less than 1, similarly to the respective values for methacrylates in

**Table II** Experimental Data for the Copolymerization of St ( $M_1$ ) with *N*-VC ( $M_2$ ) at 60°C in the Presence of AIBN (0.5% by Wt) in Ethyl Acetate

Composition of Starting Mixture (mol %)		Polymerization Time (h)	Conversion (Wt %)	Polymerization Rate (Wt %)	N Content in Copolymer (Wt %)	Fraction of <i>N</i> -VC in Copolymer (mol %)	Mean Sequence Length	
$M_1$	$M_2$						$\mu_1$	$\mu_2$
90	10	4.50	4.01	0.89	0.26	2.04	244.49	1.00
80	20	4.17	3.06	0.73	0.58	4.48	109.31	1.01
70	30	4.17	2.89	0.69	0.97	7.69	61.97	1.01
60	40	4.00	5.17	1.29	1.41	11.43	40.35	1.02
50	50	4.17	6.33	1.52	2.00	16.08	27.51	1.02
40	60	3.83	5.23	1.37	2.45	21.28	19.79	1.03
30	70	4.00	6.69	1.67	3.14	29.31	13.25	1.05
20	80	3.83	6.50	1.70	3.94	39.12	8.91	1.07
10	90	4.50	15.12	3.36	4.83	52.19	5.65	1.12

Total monomer concentration: 2.145 mol/L.

**Table III Experimental Data for the Copolymerization of St ( $M_1$ ) with  $N$ -VC ( $M_2$ ) at 60°C in the Presence of AIBN (0.5% by Wt) in Acetone**

Composition of Starting Mixture (mol %)		Polymerization Time (h)	Conversion (Wt %)	Polymerization Rate (Wt %)	N Content in Copolymer (Wt %)	Fraction of $N$ -VC in Copolymer (mol %)	Mean Sequence Length	
$M_1$	$M_2$						$\mu_1$	$\mu_2$
90	10	3.83	5.58	1.46	0.26	1.97	277.62	1.00
80	20	4.08	5.50	1.35	0.55	4.24	126.33	1.01
70	30	4.00	5.41	1.35	0.92	7.27	71.79	1.01
60	40	3.92	3.21	0.82	1.31	10.63	47.65	1.02
50	50	4.08	2.23	0.55	1.80	15.12	32.15	1.03
40	60	4.17	3.67	0.88	2.40	21.07	21.79	1.04
30	70	3.92	3.67	0.94	3.15	29.31	14.38	1.07
20	80	4.08	5.45	1.34	4.07	40.86	9.03	1.11
10	90	4.00	7.23	1.81	5.30	59.50	4.78	1.24

Total monomer concentration: 2.145 mol/L.

copolymerization with  $N$ -VC.<sup>11,12,20</sup> In Figure 4, the copolymerization curves are presented. As one can see, for the system of St with  $N$ -VC, the curves are similar for all solvents. By examining the copolymerization curves and the product of the reactivity ratios ( $r_1 \cdot r_2$ ; see Table V), one can expect the copolymers of St with  $N$ -VC formed in all solvents to be random with a tendency to alternate.

From the values of  $r_1$  and  $r_2$ , the mean sequence length ( $\mu_1$  for St and  $\mu_2$  for  $N$ -VC) was calculated from the formulas,<sup>21</sup>  $\mu_1 = 1 + r_1[m_1]/[m_2]$  and  $\mu_2 = 1 + r_2[m_2]/[m_1]$ , where  $[m_1]$  and  $[m_2]$  are the monomer concentrations in the copolymer. The re-

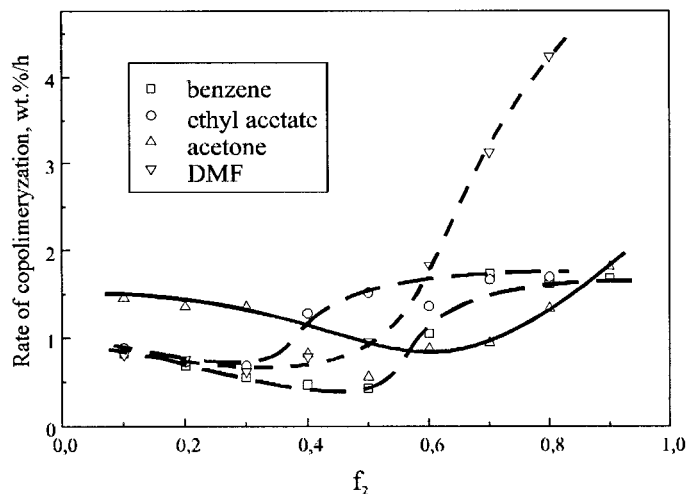
sults of calculation values are presented in Tables I–IV. The mean sequence length  $\mu_1$  and  $\mu_2$  change with the amount of St and  $N$ -VC in the feed and depend on the solvent used. The value of  $\mu_1$  varied from 3.9–140 for benzene to 6–380 for DMF and increased with increasing content of St in the feed. The mean sequence lengths of  $N$ -VC,  $\mu_2$ , varied from 1.0 to about 1.2 with increasing  $N$ -VC feed concentration in all solvents. This relatively low mean sequence length correlates with low values of  $r_2$  and confirms the alternating tendency of the St– $N$ -VC copolymers.

The copolymerization parameters  $Q_2$  and  $e_2$  for

**Table IV Experimental Data for the Copolymerization of St ( $M_1$ ) with  $N$ -VC ( $M_2$ ) at 60°C in the Presence of AIBN (0.5% by Wt) in DMF**

Composition of Starting Mixture (mol %)		Polymerization Time (h)	Conversion (Wt %)	Polymerization Rate (Wt %)	N Content in Copolymer (Wt %)	Fraction of $N$ -VC in Copolymer (mol %)	Mean Sequence Length	
$M_1$	$M_2$						$\mu_1$	$\mu_2$
90	10	4.00	3.23	0.81	0.20	1.51	383.16	1.00
80	20	3.83	2.91	0.76	0.52	4.00	141.31	1.01
70	30	4.17	2.59	0.62	0.91	7.19	75.53	1.01
60	40	4.00	3.18	0.79	1.39	11.35	46.70	1.02
50	50	3.92	3.76	0.96	1.93	16.37	30.88	1.03
40	60	4.08	7.48	1.83	2.56	22.75	20.85	1.05
30	70	3.58	11.20	3.13	3.27	30.72	14.19	1.07
20	80	3.66	15.53	4.24	4.06	40.73	9.51	1.11
10	90	3.92	15.86	4.05	4.95	53.76	6.03	1.19

Total monomer concentration: 2.145 mol/L.



**Figure 1** Rate of copolymerization (Wt %/h) for the system St/*N*-VC vs. mol fraction ( $M_2$ ) in the feed in different organic solvents at 60°C.

the *N*-VC monomer, which are estimated from the Alfrey–Price equation,<sup>13</sup> are summarized in Table V. It is well known that the reactivity of comonomers are strongly influenced by the type of comonomer and the polymerization medium, and different results can be found by different methods. These values in all solvents were calculated from the reactivity ratios  $r_1$  and  $r_2$  obtained by the RREVM program and from the literature for  $Q_1$  and  $e_1$  for St (Ref. 22) ( $Q_1 = 1.0$ ,  $e_1 = -0.8$ ). The

values of  $Q_2$  and  $e_2$  obtained in this work differ significantly from one another as well as from the literature value for *N*-VC ( $Q = 0.26$ ,  $e = -1.29$ ).<sup>20</sup> These differences result from the varying polymerization medium used and confirm the influence of the solvent on the reactivity of both monomers in the copolymerization reaction. The values of  $e_2$  for *N*-VC are negative and significantly higher in magnitude than those obtained by other authors.<sup>12,20</sup> These negative values of  $e_2$  reflect the

**Table V** Reactivity Ratios of St ( $r_1$ ) with *N*-VC ( $r_2$ ) in Various Solvents and  $Q_2$  and  $e_2$  Values for *N*-VC

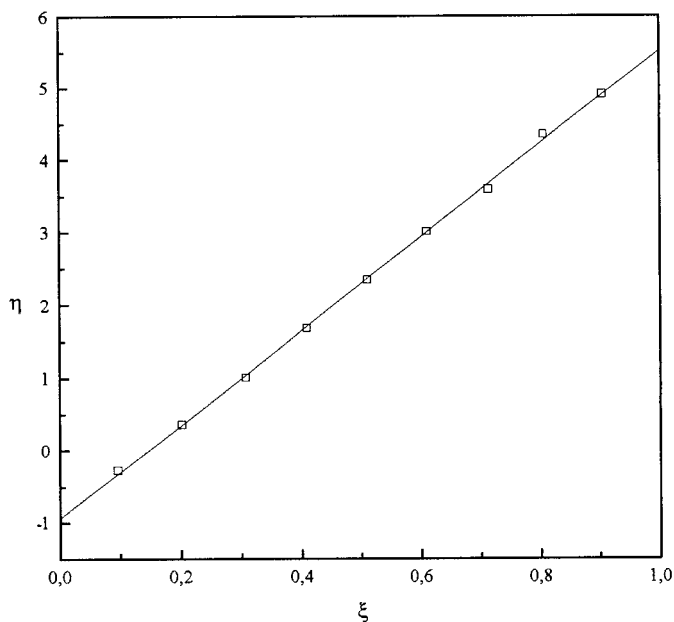
Solvent	$\mu^a$ [D]	$\delta^b$ [MPa <sup>1/2</sup> ]	$r_1 \times r_2$	F–R	K–T [I]	K–T [II]	RREVM	$Q_2$	$e_2$	$Q_1^c$	$e_1^c$
Benzene	0.00	18.8	$r_1$	4.01	3.84	3.79	3.74	0.51	-1.60	1.17	-0.25
			$r_2$	0.23	0.42	0.35	0.14				
			$r_1 \times r_2$	0.91	1.63	1.33	0.52				
Ethyl acetate	1.78	18.6	$r_1$	5.13	5.08	5.19	5.02	0.37	-1.57	0.62	-0.80
			$r_2$	0.17	0.34	0.26	0.11				
			$r_1 \times r_2$	0.85	1.71	1.34	0.55				
Acetone	2.71	18.8	$r_1$	5.54	5.52	5.31	5.50	0.24	-1.16	0.66	0.01
			$r_2$	0.16	0.40	0.34	0.16				
			$r_1 \times r_2$	0.90	2.22	1.82	0.88				
DMF	3.82	24.8	$r_1$	7.19	5.36	5.25	5.83	0.23	-1.17	0.65	-0.57
			$r_2$	0.49	0.39	0.26	0.17				
			$r_1 \times r_2$	3.54	2.09	1.39	0.99				

<sup>a</sup> Dipole moment ( $\mu$ ).

<sup>b</sup> Solvent solubility parameter ( $\delta$ ).

<sup>c</sup> Data for ethyl methacrylate.

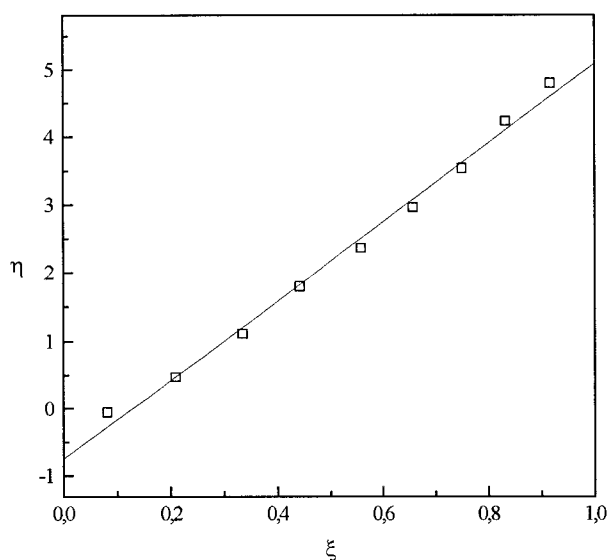
<sup>d</sup> Data for butyl methacrylate.



**Figure 2** Plot of  $\eta$  vs.  $\xi$  for the system St/N-VC in ethyl acetate. Kelen-Tüdös method (I);  $r_1 = \eta(1)$ ;  $-r_2/\alpha = \eta(0)$ ,  $\alpha = 0.1715$ , where  $\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha$ ;  $\alpha = \sqrt{F_m F_M}$ .  $F_m$  and  $F_M$  are the lowest and highest values from the experimental data, respectively.

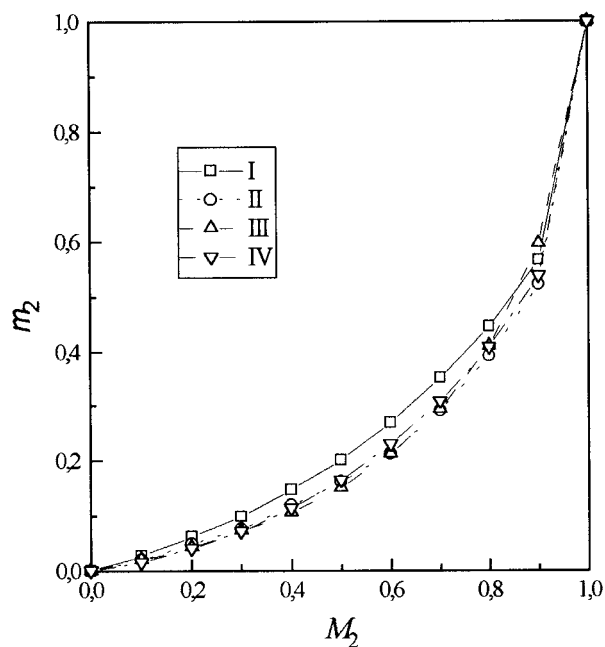
donor interaction of the carbazole ring with the vinyl group of styrene. These mutual interactions are localized on the  $C_\beta$  atom of N-VC, causing the more negative formal charge as compared with that of the  $C_\beta$  atom in St.

The values of  $Q_2$  and  $e_2$  were used to calculate



**Figure 3** Plot of  $\eta$  vs.  $\xi$  for the system St/N-VC in acetone. Kelen-Tüdös method (I);  $r_1 = \eta(1)$ ;  $-r_2/\alpha = \eta(0)$ ,  $\alpha = 0.1715$ , where  $\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha$ ;  $\alpha = \sqrt{F_m F_M}$ .  $F_m$  and  $F_M$  are the lowest and highest values from the experimental data, respectively.

$Q_1$  and  $e_1$  for ethyl and butyl methacrylates, for which the reactivity ratios  $r_1$  and  $r_2$  in copolymerization with N-VC were determined earlier in the



**Figure 4** Relationship between the mol fraction of N-VC in the feed ( $M_2$ ) and mol fraction in the copolymer ( $m_2$ ) for the system St-N-VC in different organic solvents at 60°C. (1) Benzene; (2) ethyl acetate; (3) acetone, 4-DMF.

same solvents (for butyl methacrylate only in benzene).<sup>11</sup> These calculated values differ significantly from one another as well as from the literature data.<sup>22,23</sup>

## REFERENCES

1. A. Hippel and L. G. Wesson, *Ind. Eng. Chem.*, **38**, 127 (1946).
2. V. M. Sytyagin and V. P. Lopatynski, *Vysokomol. Soed. Ser. B.*, **23**(1), 16 (1981).
3. T. Alfrey Jr. and S. Kapur, *J. Polym. Sci.*, **4**, 215 (1949).
4. R. Hart, *Macromol. Chem.*, **47**(1), 143 (1961).
5. A. Ledwith, G. Galli, E. Chiellini, and R. Solaro, *Polym. Bull.*, **1**, 491 (1979).
6. L. L. Gainceva, G. N. Kurov, E. I. Zhovtyi, T. V. Merlina, and G. G. Skvorcova, *Vysokomol. Soed. Ser. B.*, **30**(2) (1988).
7. I. Negulescu, D. Feldman, and Cr. Simunescu, *Polymer*, **13**, 149 (1972).
8. T. Sato, M. Abe, and T. Otsu, *Macromol. Chem.*, **178**, 1259 (1977).
9. J. C. Bevington, C. J. Dyball, and J. Leech, *Macromol. Chem.*, **180**, 657 (1979).
10. A. Rytzel, *Acta Polym.*, **41**(5), 289 (1990).
11. A. Rytzel, *J. Appl. Polym. Sci.*, **45**, 1911 (1992).
12. R. Chrzęszcz and J. Pielichowski, *Polimery (Warsaw)*, **40**(7-8), 458 (1995).
13. T. Alfrey, Jr. and C. C. Price, *J. Polym. Sci.*, **2**, 101 (1947).
14. M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 259 (1950).
15. T. Kelen and F. Tüdös, *React. Kinet. Catal. Lett.*, **1**(4), 487 (1974).
16. T. Kelen, F. Tüdös, T. Földes-Berezhnykh, and B. Turcanyi, *React. Kinet. Catal. Lett.*, **2**(4), 439 (1975).
17. T. Kelen and F. Tüdös, *J. Macromol. Sci. Chem. A*, **9**, 1 (1975).
18. M. Dube, R. Amin Sanayei, A. Penlidis, K. F. O'Driscoll, and P. M. Reilly, *J. Polym. Sci. Part A. Polym. Chem.*, **29**, 703 (1991).
19. F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).
20. R. Z. Greenley, *J. Macromol. Sci.-Chem. A*, **9**(4), 505 (1975); **14**(4), 427 (1980).
21. C. W. Pyun, *J. Polym. Sci. Part A-2 Polym. Phys.*, **8**, 1111 (1970).
22. I. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, 3rd ed., Wiley, New York, 1989, Vol. II, p. 267.
23. E. C. Leonard, *Vinyl and Diene Monomers*, Wiley, New York, 1970, Part I, p. 189.