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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article talpur, Mir Munsif Ali and Kaim, Andrzej(1995) 'Investigation of Acrylamide-Styrene Copolymerization System in Cyclohexanone in the Absence of a Conventional Radical Initiator', Journal of Macromolecular Science, Part A, 32: 2, 241 – 249

To link to this Article: DOI: 10.1080/10601329508011159

URL: <http://dx.doi.org/10.1080/10601329508011159>

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INVESTIGATION OF ACRYLAMIDE–STYRENE COPOLYMERIZATION SYSTEM IN CYCLOHEXANONE IN THE ABSENCE OF A CONVENTIONAL RADICAL INITIATOR

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Key Words: Acrylamide; Styrene; Copolymerization; Active hydrogen atom

ABSTRACT

Copolymerization of the acrylamide–styrene system has been studied at 75°C in the absence of any conventional radical in dioxane, cyclohexanone, cyclohexanone/dioxane, and cyclohexanone/benzene mixtures. The reactivity coefficient values have been evaluated by YBR, KT, and EVM methods. The polarity and strong hydrogen bonding ability of the reaction medium with the amide group of the acrylamide affects the reactivity ratio values by disturbing the keto/enol equilibrium of the acrylamide. A comprehensive comparative study of the r -parameters achieved for these copolymer systems with the reactivity coefficient values of the same monomer system initiated by the conventional free-radical initiator has been presented. From the r -product values obtained by the EVM method, the following order of alternating tendency of the monomers in copolymers prepared in different media was found: cyclohexanone/benzene mixture > dioxane > cyclohexanone/dioxane mixture > cyclohexanone. The kinetic results obtained confirm the specific interactions between acrylamide and cyclohexanone.

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INTRODUCTION

The radical homopolymerization of several polar vinyl monomers in the presence of some active hydrogen atom containing compounds (e.g., aldehydes, ketones, etc.) has been the subject of many publications [1–8]. The mechanism of the reaction involving transfer of the hydrogen radical abstracted from these compounds to the monomer, originally proposed by Imoto et al. [3, 4] and Ouchi et al. [5] for the polymerization of methyl methacrylate (MMA) initiated with aldehydes and later discussed for the polymerization of MMA started by cyclohexanone, still remains uncertain for many reasons. For example, the so-called thermal polymerization of MMA, most probably always simultaneously present in all the investigated polymerization systems containing MMA and itself still under discussion (9–11) complicates very much the kinetic [7] and spectral analysis [4] of the investigated reaction.

For this reason the proof of the mechanism using electron paramagnetic resonance (EPR) reported by Sato [2] and Ouchi [5] seems to be indecisive [12]. Moreover, we suspect that compounds with active hydrogen atoms can undergo some thermal transformations liberating radicals which can initiate the polymerization, e.g., the thermal radical self-condensation of cyclohexanone [13].

We have recently been studying the initiating activity of these compounds in the copolymerization system containing methyl methacrylate copolymerized with styrene [14, 15]. In the present monomer system MMA has been replaced in the pair with styrene by acrylamide (AAM). Acrylamide, like MMA, undergoes homopolymerization in the presence of cyclohexanone [6]. A monomer system of the same type as previously discussed [14] has been chosen to verify the activity of cyclohexanone in the copolymerization reaction.

EXPERIMENTAL

The purification of monomers, cyclohexanone, dioxane, and benzene as well as the procedure for copolymerization have been described previously [14–16]. The experimental conditions were kept the same as reported in our previous work [16].

RESULTS AND DISCUSSION

The copolymer composition data for AAM–Sty in different solvents are listed in Tables 1–4 together with corresponding weight-% conversion.

The AAM–Sty copolymerization curves as a function of monomer feed versus copolymer composition are shown in Fig. 1 and refer to the thermal copolymerization in dioxane as well as copolymerization of monomers in cyclohexanone, cyclohexanone/dioxane (1:1.16 in volume) mixture and cyclohexanone/benzene (1:1.16 in volume) mixture at 75°C in the absence of any conventional radical initiator.

The analytical data (percent nitrogen) of the copolymers obtained have been used to determine the r -parameters. The reactivity ratios of AAM (r_1) and Sty (r_2) for all the investigated copolymerization systems were calculated by Yezerielev, Brokhina, and Roskin method (YBR method) [17], Kelen and Tüdös method (KT

TABLE 1. Copolymerization of Acrylamide (M_1) and Styrene (M_2) at 75°C in the Presence of Dioxane

Mole fraction in feed		Reaction time, minutes	Conversion weight, %	Results of elemental analysis of copolymer			Mole fraction M_1 in copolymer
M_1	M_2			N, %	C, %	H, %	
0.90	0.10	240	1.722	14.67	4.360	7.580	0.810
0.80	0.20	240	1.780	13.42	5.980	7.030	0.758
0.70	0.30	240	1.630	12.29	6.590	6.695	0.709
0.60	0.40	240	1.580	10.98	8.685	7.055	0.649
0.50	0.50	270	1.560	9.030	9.910	6.740	0.554
0.40	0.60	280	1.230	7.305	3.885	7.355	0.463

TABLE 2. Copolymerization of Acrylamide (M_1) and Styrene (M_2) at 75°C in the Presence of Cyclohexanone

Mole fraction in feed		Reaction time, minutes	Conversion weight, %	Results of elemental analysis of copolymer			Mole fraction M_1 in copolymer
M_1	M_2			N, %	C, %	H, %	
0.90	0.10	240	6.360	13.810	8.385	8.010	0.870
0.80	0.20	240	4.274	13.335	1.830	7.565	0.754
0.70	0.30	240	2.780	11.395	3.170	6.765	0.668
0.60	0.40	240	2.332	10.435	8.795	7.075	0.623
0.50	0.50	360	2.080	8.365	3.590	7.380	0.519
0.40	0.60	420	1.300	6.250	8.575	7.105	0.405

TABLE 3. Copolymerization of Acrylamide (M_1) and Styrene (M_2) at 75°C in the Presence of Cyclohexanone/Dioxane (1:1.16 by volume) Mixture

Mole fraction in feed		Reaction time, minutes	Conversion weight, %	Results of elemental analysis of copolymer			Mole fraction M_1 in copolymer
M_1	M_2			N, %	C, %	H, %	
0.90	0.10	240	5.390	15.520	49.335	7.200	0.845
0.80	0.20	240	4.307	14.180	54.830	7.305	0.790
0.70	0.30	240	3.023	12.430	57.205	7.120	0.715
0.60	0.40	240	2.979	10.960	63.285	7.350	0.648
0.50	0.50	330	2.446	8.961	67.000	7.285	0.550
0.40	0.60	330	1.961	6.947	82.825	7.840	0.444

TABLE 4. Copolymerization of Acrylamide (M_1) and Styrene (M_2) at 75°C in the Presence of Cyclohexanone/Benzene (1:1.16 by volume) Mixture

Mole fraction in feed		Reaction time, minutes	Conversion weight, %	Results of elemental analysis of copolymer			Mole fraction M_1 in copolymer
M_1	M_2			N, %	C, %	H, %	
0.90	0.10	240	4.600	14.82	43.025	7.310	0.817
0.80	0.20	260	3.800	13.45	47.675	7.455	0.759
0.70	0.30	260	2.700	13.42	47.730	7.315	0.751
0.60	0.40	330	2.181	12.23	50.886	7.417	0.706
0.50	0.50	420	2.020	11.07	55.615	6.845	0.653
0.40	0.60	420	1.103	9.445	60.110	6.930	0.574

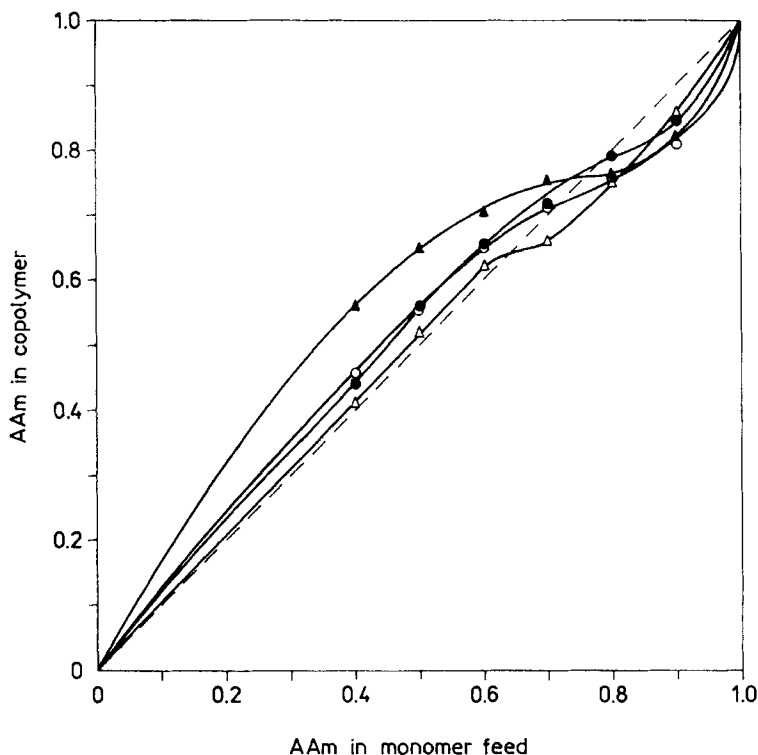


FIG. 1. Copolymerization of acrylamide (r_1) and styrene (r_2) at 75°C. Reaction medium: (○) dioxane; (△) cyclohexanone; (●) cyclohexanone/dioxane (1:1.16 by volume) mixture; (▲) cyclohexanone/benzene (1:1.16 by volume) mixture.

method) [18] and by the method using the Error-In-Variable Model (EVM method) [19]. Reactivity parameters were generated using random errors of 5 and 1% for the monomer feed composition and copolymer composition, respectively, with the EVM method. The reactivity coefficient data estimated by the above-mentioned methods for all the copolymerization systems investigated are reported in Table 5. It is worth mentioning that different methods for calculating the r -parameters offer different values for the same set of experimental data [20, 21]. For the systems investigated this statement is even more evident as shown in Table 5. For comparison with the literature, however, we have applied almost all of the most popular calculation methods.

The thermal copolymerization of AAm and Sty does not proceed in benzene; however, it does proceed in dioxane. The r -parameter data for the copolymerization of AAm with Sty in dioxane or in any other solvent in the absence of a conventional radical initiator could not be found in the literature. The reported [22] r -parameter values evaluated by the FR method as well as those recalculated by Greenly [20] by the KT method for the copolymerization of the present monomer system in dioxane initiated by a free-radical initiator are $r_1(\text{AAm}) = 1.38$ (FR) and 1.325 (KT), and $r_2(\text{Sty}) = 1.27$ (FR) and 1.208 (KT); they do not match our results calculated by the same method. The absence of a conventional free radical leads to smaller r -parameter values. The higher r_1 than r_2 is interesting, but thermal homopolymerization of AAm does not proceed in dioxane [6]. The explanation for the nonappearance of the thermal homopolymerization of AAm can be the very low rate of reaction, thus it is not observed under the conditions used compared with the rate of thermal copolymerization of Sty with polar vinyl monomers which is much faster [23]. The reason for the higher r_1 value as compared to the r_2 value in dioxane may be explained on the basis of the strong hydrogen bonding ability of dioxane to the amide group [24] that is assumed to affect AAm monomer association [25] and

TABLE 5. The r_1 (AAm) and r_2 (Sty) Values Calculated by Different Methods in Various Reaction Media at 75°C in the Absence of Any Conventional Initiator

Reaction medium	r -values	YBR method	KT method	EVM method
Dioxane	r_1	0.43 ± 0.03	0.45 ± 0.08	0.61
	r_2	0.01 ± 0.07	0.06 ± 0.08	0.34
Cyclohexanone	r_1	0.62 ± 0.05	0.67 ± 0.06	0.72
	r_2	0.38 ± 0.10	0.58 ± 0.06	0.68
Cyclohexanone/dioxane (1:1.16 by volume) mixture	r_1	0.58 ± 0.09	0.61 ± 0.08	0.77
	r_2	0.26 ± 0.20	0.23 ± 0.08	0.50
Cyclohexanone/benzene (1:1.16 by volume) mixture	r_1	0.42 ± 0.07	0.45 ± 0.10	0.69
	r_2	-0.23 ± 0.15	-0.29 ± 0.10	0.012

consequently disturbs the keto/enol equilibria of AAm [22], which raises vinyl bond activity in the copolymerization reaction. Due to the lack of any opportunity for a hydrogen bridge, the Sty monomer and its radical remain comparatively unchanged in this environment. The source of radicals in the thermal copolymerization of AAm and Sty can be both monomers; however, the contribution of the Sty is higher because it homopolymerizes in dioxane [6].

The product value of r_1 and r_2 calculated by the EVM method is 0.2056, which suggests there is an alternating tendency for the monomers in the copolymer.

The copolymerization of acrylamide and styrene was performed in cyclohexanone (pure) in the absence of any conventional radical initiator. The r -parameters for the present system as calculated by the KT method are different from the values reported by Leoni et al. [26] as well as the values recalculated by the corresponding method by Greenly [20]. The r_1 values evaluated by the YBR and EVM methods are in reasonable agreement with the r_1 data for the same monomer system initiated by the free-radical initiator in the dioxane/ethanol (70/30 in volume) mixture [22] and the in water/*tert*-butyl alcohol (50/50 in volume) mixture [24]; however, the r_2 values are different.

All the methods give higher r -parameter values for AAm and Sty in cyclohexanone than the reactivity ratio values obtained in dioxane. The r_2 values are much different. The higher r -parameter data can be interpreted [24] on the basis of polar-polar interactions between cyclohexanone and the highly polar amide group of AAm. This results in the same effects as the hydrogen bonding effects mentioned above. Because cyclohexanone is highly polar and has a high dielectric constant value [27], it can shift the keto/enol equilibrium of the amide molecule which is dependent on the dielectric constant and the polarity of the solvent.

The product of r_1 and r_2 data calculated by the EVM method is 0.4874. This value is higher than the r -product data for the monomers in dioxane.

The copolymerization of the monomers was carried out in a cyclohexanone/dioxane (1:1.16 in volume) mixture in the absence of a conventional radical initiator. The r -parameters are reported in Table 5. The r_1 value calculated by the KT method is in reasonable agreement with the data reported by Greenly [20] recalculated from the experimental data of Leoni et al. [26] by the corresponding method, but the r_2 values do not match. Furthermore, the r_1 data generated by the YBR and EVM methods are in good agreement with the r_1 values calculated by the FR method for the copolymerization of the present monomer system initiated by a free-radical initiator in dioxane/ethanol (70/30 in volume) mixture [22] and in water/*tert*-butyl alcohol (50/50 in volume) mixture [24]; however, the calculation methods are different. The r_2 values are smaller and do not fit with the free-radical-initiated copolymerization of monomers [22]. The r_2 value evaluated by the YBR method is in reasonable agreement with the r_2 value reported by Minsk et al. [24] for the free-radical copolymerization of the same monomer pair; however, the calculation methods are different. The reason why the copolymers are richer in acrylamide can be explained by the ability of dioxane to form hydrogen bonds with the amide group [24]. On the other hand, cyclohexanone, which is highly polar [27], has polar-polar interactions with the highly polar amide group of AAm. As mentioned above, it is a well-known fact [24] that polar-polar interactions and hydrogen bridging produce the same effects. In our case, both factors operate simultaneously. Styrene,

on the contrary, has a low dipole moment and lacks opportunity to form a hydrogen bridge. Therefore, Sty and its radical are expected to remain relatively unchanged.

The r -parameter values calculated by the EVM method for AAm and Sty in cyclohexanone/dioxane (1:1.16 in volume) mixture are higher than in dioxane. On the other hand, comparison with the reactivity coefficient data obtained in cyclohexanone shows that the r_1 values are a good match while the r_2 values are smaller in the cyclohexanone/dioxane mixture. Thus, it is concluded that the reactivity of monomers increases in the presence of cyclohexanone. This increasing reactivity of monomers can be attributed to the specific interaction between acrylamide and cyclohexanone, which probably starts the copolymerization reaction.

The product of r_1 and r_2 data for the cyclohexanone/dioxane mixture estimated by the EVM method is 0.385. This value is smaller than the r -product data acquired for the monomers in cyclohexanone but larger than that obtained in dioxane.

The copolymerization of AAm and Sty was performed in the cyclohexanone/benzene (1:1.16 by volume) mixture in the absence of any conventional radical initiator. All the r_2 values except by the EVM method are negative, which obviously have no physical meaning [28]. The r -parameters estimated by all the methods do not fit with the data calculated by the FR method as reported in the literature [22, 24, 29] or as recalculated by the KT method [20] for the free-radical-initiated copolymerization of the monomer-solvents system. By comparing the results it can be seen that the r_1 value evaluated by the EVM method is in basic agreement with the data achieved for the same monomers in dioxane; r_2 is much smaller. Similarly, the r_1 value matches well whereas r_2 is higher in cyclohexanone than in the cyclohexanone/benzene mixture.

Therefore, it can be said that in a nonpolar, nonbridging solvent such as benzene, both the AAm and Sty radicals appear to polymerize, preferentially with the AAm monomer.

The product of r_1 and r_2 data estimated by the EVM method is 0.0082. This value is very much smaller than the product of r_1 and r_2 acquired for the monomers in dioxane, cyclohexanone, or the cyclohexanone/dioxane mixture. As this data is closer to zero, a very strong alternating tendency of monomers in the copolymer is suggested.

It was mentioned above that the copolymerization of AAm and Sty monomers does not proceed in benzene in the absence of any conventional radical initiator or cyclohexanone. However, when benzene is replaced in part by cyclohexanone, the copolymerization reaction starts in the absence of any conventional radical initiator as illustrated in Fig. 2. It is clearly evident from the data in Fig. 2 that the rate of reaction increases as the concentration of cyclohexanone and/or AAm in the reaction mixture increases, probably because of the number of active cyclohexanone molecules involved in the initiating process. This statement is supported by the molecular weight determination of the copolymer obtained. We have not determined the molecular weight in the present system; however, molecular weight investigations have been performed for the homopolymerization of methyl methacrylate initiated with cyclohexanone in which the number-average molecular weight dropped with an increasing concentration of cyclohexanone [30]. Moreover, it is also unequivocally pointed out from the data in Fig. 2 that as the molar ratio of

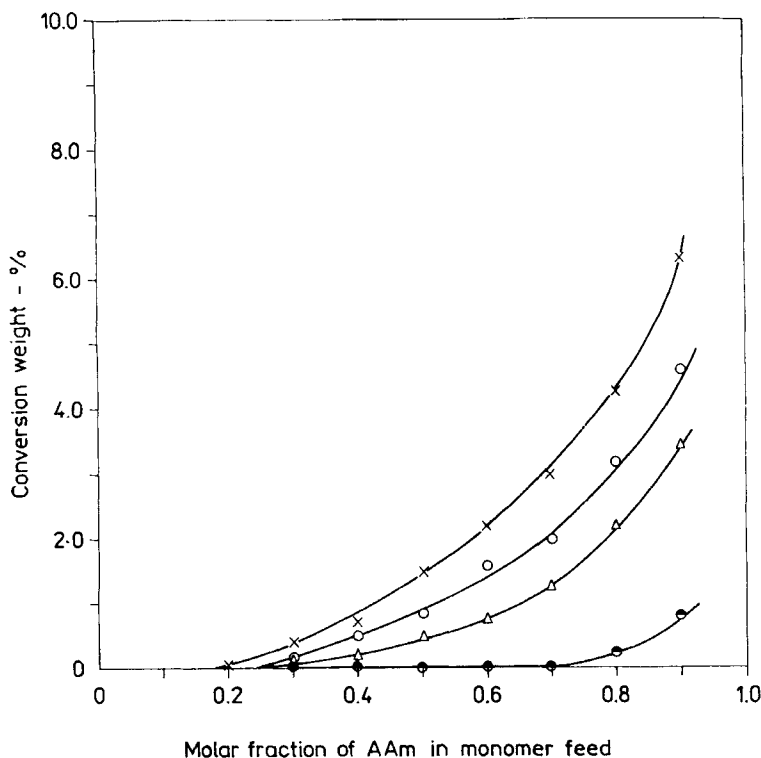


FIG. 2. Conversion of acrylamide-styrene system vs mole fraction of acrylamide in monomer feed in the presence of different concentrations of cyclohexanone [Chn], at 75°C, reaction time 4 hours: [Chn] = 0 mol·dm⁻³, no copolymer; (○) [Chn] = 0.09 mol·dm⁻³; (△) [Chn] = 0.26 mol·dm⁻³; (●) [Chn] = 0.44 mol·dm⁻³; (×) [Chn] = 0.79 mol·dm⁻³.

AAM in the monomer feed composition lessens, the conversion of monomers to copolymer diminishes and it becomes zero at a 0.2 molar ratio of AAm in the monomer feed.

CONCLUSIONS

Except for the residual thermal copolymerization of monomers in dioxane, the presence of cyclohexanone in the reaction system starts the copolymerization reaction of the acrylamide-styrene system. A similar mechanism is proposed for the system containing methyl methacrylate and cyclohexanone which probably proceeds by the abstraction of an active hydrogen atom by AAm from cyclohexanone.

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Received March 11, 1994

Revision received June 3, 1994