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*Polymer Science U.S.S.R.* Vol. 26, No. 4, pp. 780-788, 1984  
 Printed in Poland

0032-3950/84 \$10.00+.00  
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## GENERAL NATURE OF THE EFFECT OF MOLECULAR WEIGHT ON THE COMPOSITION OF A COPOLYMER ON HOMOGENEOUS RADICAL COPOLYMERIZATION\*

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(Received 15 July 1982)

The authors have studied the dependence of the composition of a copolymer on *M* or intrinsic viscosity on radical copolymerization of styrene with acrylonitrile and methacrylic acid. The composition of the copolymer is found to depend on the concentration of radical initiator or chain transfer agent (RSH, CBr<sub>4</sub>, substituted silicon hydrides) as demonstrated by direct experiments on fractionation of the copolymers of initial conversion, from which it

\* *Vysokomol. soyed.* **A26**: No. 4, 704-710, 1984.

follows that the latter differ fundamentally in composition. The general nature of the effect is demonstrated in experiments on the influence of the concentration of the radical initiator on the composition of the copolymer and the magnitudes  $r_1$  and  $r_2$ . The dependence is found on homogeneous copolymerization of styrene with methacrylic acid, acrylonitrile, vinyl acetate, vinylidene chloride; vinyl acetate with vinylidene chloride and 2-methyl-5-vinyl pyridine; and methylmethacrylate with vinylidene chloride.

EARLIER we reported on an unusual phenomenon discovered in the field of homogeneous radical copolymerization and consisting in the fact that for a number of systems the composition of the copolymer at the initial stage of conversion is found to depend on its  $M$  [1, 2] which was regulated by changing the concentration of the radical initiator or by introducing into the system molecular weight regulators. Obviously, these facts go beyond the existing theory of radical copolymerization and point to the presence of hitherto disregarded factors influencing the formation of the copolymer chain. To evaluate the importance and interpret the causes of the phenomenon discovered the first task was to determine whether it was of a general character. This problem is considered in the present paper.

The technique of purifying the monomers, solvents, initiators and polymers and the technique of analysing the composition of the copolymers styrene-methacrylic acid (MAA), acrylonitrile (AN)-styrene and 2-methyl-5-vinyl pyridine (MVP)-vinyl acetate (VA) are described in references [3-5]. The styrene-VA copolymers were purified by precipitation from benzene with petroleum ether and analysed by IR spectroscopy [6]. The composition of the copolymer vinylidene chloride (VDC) with styrene and VA was analysed from the chlorine content [7].

Polymerization was carried out in bulk at 313-353 K to 5-7% conversion. Initiation was with DAA, benzoyl peroxide (BP) and dicyclohexylperoxidicarbonate (DCC). The styrene-MAA copolymer was fractionated by fractional precipitation from 1% acetone-methanol solution with a mixture of sulphuric and petroleum ethers at 293-295 K and the AN-styrene copolymer from a 1% solution of methylethylketone with methanol [8]. The characteristic viscosity of the styrene-MAA copolymer was measured in dioxane at 303 K and the AN-styrene copolymer and its fractions in methylethylketone at 303 K. The  $M$  values of the AN-styrene copolymer and its fractions were calculated from the formula in reference [9]. The boundaries of the homophase and heterophase regions of copolymerization of styrene-MAA were determined from the light scatter with the FPS-3M instrument and from light transmission with the FEKN-54 instrument.

Let us take a closer look at the essence of the phenomenon discovered with reference to the copolymerization of styrene with MAA and AN. As is clear from Figs. 1-3 increase in the concentration of the radical initiator and chain transfer agent leads to sym-batic change in the composition and intrinsic viscosity of the copolymers [7]. The data in these figures may be represented in the form of the dependence of composition on  $[\eta]$  which points to an undoubted correlation between these characteristics of the position of the copolymer of the radical initiator or chain transfer agent does not depend on their nature. Thus, such initiators as DAA and BP influence roughly to an equal (though different) degree the composition of the copolymers styrene-MAA (Fig. 1) and VP-VA [2]; this effect is also found for DCC for the systems VDC-MMA [2] and styrene-AN (Fig. 3). Likewise such  $M$  regulators as RSH,  $CBr_4$ ,  $(C_6H_5)_3GeH$

and substituted silicon hydrides similarly influence the composition of the copolymers MAA [1-4], vinyl pyridines [2, 5] and AN (Fig. 3) with vinyl monomers.\*

For the system styrene-MAA and some others the value  $[\eta]$  is given as the magnitude characterizing  $M$  of the copolymer. This leads to a certain ambiguity since  $[\eta]$  of the copolymer may depend not only on its  $M$  but also on the composition. However, we consider that the observed interval of change in  $[\eta]$  (from 0.15 to 0.05 m<sup>3</sup>/kg, Fig. 1) cannot be due merely to change in the composition of the copolymer (from 61 to 50 mole % MAA) and is essentially linked with fall in its  $M$  as a result of increase in the content of radical initiator or chain transfer agent during synthesis. In addition, it has proved possible to calculate directly the values of  $M$  for the styrene-AN copolymer [9].

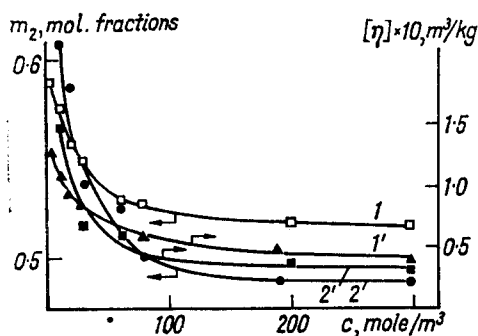


FIG. 1

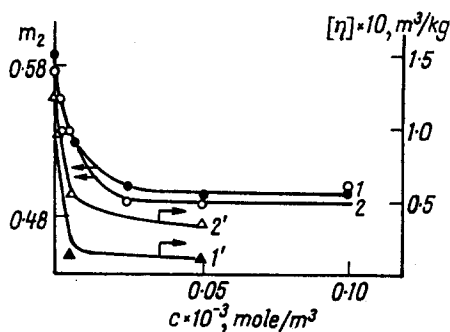


FIG. 2

FIG. 1. Dependence of  $m_2$  and  $[\eta]$  of copolymer styrene-MAA ( $M_2=0.5$ ) on concentration of the initiators DAA (1, 1') and BP (2, 2') at 333 K;  $m_2$  is the content of MAA units in the copolymer; 1', 2' - dioxane, 303 K.

FIG. 2. Dependence of  $m_2$  and  $[\eta]$  of copolymer styrene-MAA ( $M_2=0.5$ ) on concentration of the chain transfer agent  $\text{CBr}_4$  (1, 1'),  $(\text{C}_6\text{H}_5)_3\text{GeH}$  (2, 2');  $[\text{DAA}]=12 \text{ mole/m}^3$ , 333 K; 1', 2' - dioxane, 303 K.

Thus, the most general formulation of the phenomenon as dependence of the composition of the copolymer on its  $M$  at the initial stage of homogeneous radical copolymerization seems to us quite correct. Such a formulation has a most important implication. Since the  $M$  distribution is characteristic of copolymers as it is of homopolymer molecules, then despite existing notions it is to be expected that copolymers at initial conversion may differ in composition. To check this assumption we subjected to fractionation the copolymers styrene-MAA and styrene-AN obtained by homogeneous radical copolymerization to 5% conversion. It was found that the two copolymers fundamentally differ in composition (Tables 1-3) with a quite definite correlation being observed between the composition and  $M$  of the fractions very close to that observed on regulation

\* Some of these regulators display the functions of complexants which also leads to change in the composition of the copolymer. For details see reference [1].

of the composition and  $M$  of the copolymers by changing the concentration of the transfer agents and initiators (Figs. 4 and 5).

As well as those mentioned the MVP-VA copolymer was also found to differ in composition at initial conversion. The copolymer of composition 0.86 MVP-0.14 VA was separated by fractionation into six fractions with a content of 90 to 73 mole % MVP.

The results outlined find indirect confirmation in the published data. Thus, it was reported [10] that the composition distribution of the copolymers styrene-vinyl stearate and vinyl chloride-vinyl stearate is much wider than that expected (on the basis of calculations for given  $r_1$ ,  $r_2$ ), with a quite clear correlation being observed between the  $M$  and composition of the copolymers.

The next step was to establish the nature of the phase state of those systems for which the above described relations had been observed. For this we studied in detail the systems styrene-MAA and styrene-AN (Figs. 6 and 7). The boundaries between the regions of heterophase and homogeneous copolymerization were judged from light transmission and light scatter of the polymerizing blends. From the results it may be safely stated that the effect of dependence of the composition of the copolymer on the concentration of the initiator is observed both in heterophase and genuine homogeneous copolymerization.

TABLE 1. COMPOSITION AND INTRINSIC VISCOSITY OF THE FRACTIONS OF THE COPOLYMER STYRENE :  
: MAA = 80 : 20 mole % AT 333 K

(System solvent-precipitant: acetone + methanol - sulphuric + petroleum ethers)

$c_{DAA}$ , mole/m <sup>3</sup>	Fraction, No.	Mass of fractions		$m_2$ , mole %	$[\eta] \times 10$ , m <sup>3</sup> /kg
		$\alpha \times 10^4$ kg	%		
5	1	5.00	17.6	39.36	1.35
	2	10.00	32.1	38.49	1.05
	3	5.00	17.6	37.13	0.87
	4	3.60	12.0	36.80	0.79
	5	3.00	9.6	35.77	0.65
	6	1.50	4.8	33.15	0.49
	7	1.25	4.0	30.56	0.38
	Residue	—	—	—	—
	Total	29.40	97.7	—	—
	Non-fractionated sample	—	—	38.39	0.86
200	1	8.30	20.74	39.31	0.51
	2	6.10	15.24	38.69	0.42
	3	6.27	16.69	36.95	—
	4	4.50	11.24	36.35	0.36
	5	4.65	11.62	33.80	0.32
	6	2.41	6.02	33.04	0.30
	7	1.70	4.25	31.48	0.28
	8	1.32	3.30	30.04	—
	9	1.75	4.37	29.70	0.24
	Residue	1.80	4.65	—	—
	Total	38.80	97.0	—	—
	Non-fractionated sample	—	—	37.2	0.30

It is important to note that in the concentration region of the monomers corresponding to the latter the coefficient of asymmetry ( $I_{45}/I_{135}$ ) regularly rises with increase in the content of MAA in the blend. This points to rise in the anisotropy of the solution due to fall in the thermodynamic affinity of the copolymer formed and monomeric reaction blend leading to aggregation of the polymer coils.

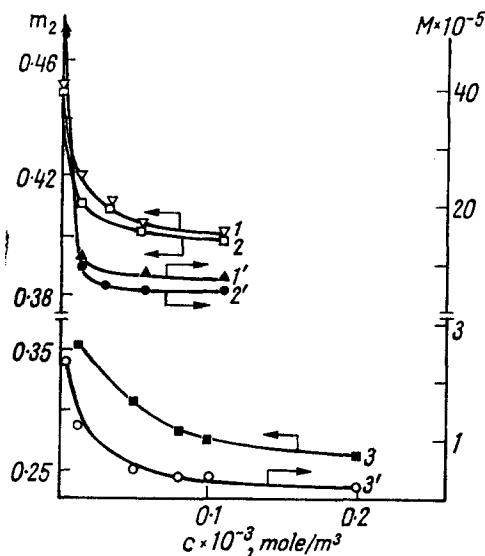


FIG. 3

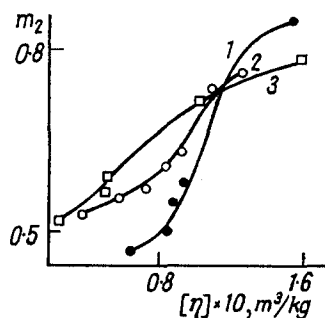


FIG. 4

FIG. 3. Dependence of  $m_2$  and  $M$  of copolymer AN-styrene on concentration of the chain transfer agent and initiator ( $C_6H_5$ )<sub>3</sub>GeH (1, 1'),  $CBr_4$  (2, 2'), 333 K.  $M_2=0.5$ ,  $[DAA]=12$  mole/ $m^3$ ; 3, 3'—DCC ( $M_2=0.3$ ), 313 K;  $m_2$  content of AN units in copolymer; 1'–3'—methyl ethyl ketone, 303 K.

FIG. 4. Dependence of  $m_2$  on  $[\eta]$  of samples of the copolymer styrene-MAA obtained at different concentrations of BP (1) and DAA (2) and fractions of this copolymer isolated by the method of fractional precipitation (3); 3— $[DAA]=5$  mole/ $m^3$ , 333 K;  $M_2=0.5$ ; dioxane; 303 K.

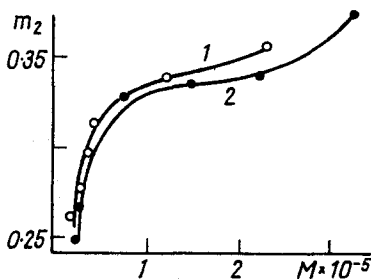


FIG. 5. Dependence of  $m_2$  on  $[\eta]$  of samples of the copolymer AN-styrene ( $M_2=0.3$ ) at different concentrations of initiator DCC (1) and fractions of this copolymer (2) isolated by the method of fractional precipitation; 2— $[DCC]=5$  mole/ $m^3$ , 313 K; methyl ethyl ketone, 303 K.  $M_2$ ,  $m_2$  is the content of AN units in monomer blend and copolymer respectively.

To establish the general nature of the phenomenon considered we studied copolymerization of nine systems: styrene with MAA, VA, AN, VDC and MMA; VA with VDC and MVP; and butylacrylate (BA)-MAA and MMA-VDC (Figs. 6 and 7, Table 4). In all cases the process was run in bulk. Copolymerization was homogeneous to very high concentrations of the polar component in the monomer blend (to 40–70 mole % MAA, AN or VDC). In the systems VA-styrene and VA-MVP copolymerization was homogeneous in the whole interval of composition of the monomer blends. For seven,

TABLE 2. COMPOSITION AND INTRINSIC VISCOSITY OF THE COPOLYMER STYRENE : MAA = 50 : 50 MOLE %  
AT 333 K  
(System solvent-precipitant: acetone+methanol-sulphuric+petroleum ethers)

$c_{DAA}$ , mole/m <sup>3</sup>	Fraction No.	Mass of fraction		$m_2$ , mole %	$[\eta] \times 10$ , m <sup>3</sup> /kg
		$\alpha \times 10^4$ , kg	%		
5	1	4.20	21.0	58.96	1.58
	2	4.50	22.5	57.50	1.03
	3	4.20	21.0	57.20	—
	4	2.40	10.5	53.20	0.51
	5	2.10	10.5	52.40	0.50
	6	0.90	4.5	50.60	0.25
	Residue	0.95	4.8		
	Total	19.25	96.8		
	Non-fractionated sample			58.10	1.095
200	1	8.00	20.0	51.47	0.53
	2	13.50	33.0	48.65	0.41
	3	8.00	20.0	48.57	0.40
	4	3.50	8.7	47.56	0.23
	5	2.00	5.0	47.60	0.23
	6	3.00	7.5	46.17	0.20
	Residue	1.00	2.8		
	Total	38.00	97.0		
	Non-fractionated sample			49.5	0.46

TABLE 3. COMPOSITION AND  $M$  OF THE FRACTIONS OF THE COPOLYMER STYRENE: AN = 70 : 30 MOLE %  
FOR  $[DCC] = 5.0$  MOLE/M<sup>3</sup> AND 333 K  
(System solvent-precipitant : methylethylketone-methanol)

Fraction No.	$m_2$ , mole % MAA	$M \times 10^{-5}$	Mass of fraction	
			$\alpha \times 10^4$ , kg	%
1	37.60	3.30	3.458	28.38
2	34.00	2.25	1.463	11.70
3	33.64	1.50	3.210	25.68
4	32.78	0.73	1.637	13.09
5	26.70	0.24	1.382	11.05
6	24.80	0.21	0.900	7.20
Total			12.131	97.10
Non-fractionated sample	33.00	1.30		

i.e. the vast majority of systems, excluding the system BA-MAA and MMA-styrene, in the region of the initial stage of homogeneous copolymerization the composition of the copolymer was found to depend on the concentration of the radical initiator with variation in the latter from 5 to 200 mole/m<sup>3</sup>. As follows from Figs. 1 and 3 the most important changes in the composition of the copolymer are observed in the concentration interval of the initiator from 1 to 10 mole/m<sup>3</sup> and therefore a content of the initiator  $\sim 100$  mole/m<sup>3</sup> is quite enough to detect the limiting changes in the composition of the copolymer. From the curves of the composition of the copolymers we determined the relative activities of the monomers (Table 4). Some of the curves of composition are presented in Figs. 6 and 7 discussed above. As may be seen from Table 4 the influence of the concentration of the initiator on the relative activities of the monomers is very considerable and well exceeds the possible errors of their determination.

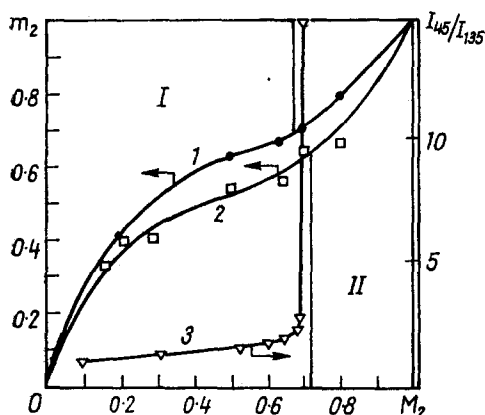


FIG. 6

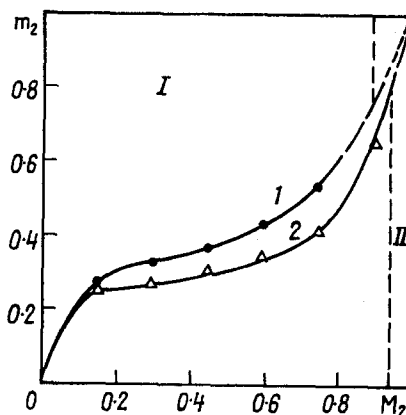


FIG. 7

FIG. 6. Curves of the composition of the copolymer styrene-MAA obtained in presence of: [BP]=5 (1) and 200 (2) mole/m<sup>3</sup> and also the dependence of the coefficient of asymmetry ( $I_{45}/I_{135}$ ) on the composition of the monomer blend styrene-MAA (3), BP=12 mole/m<sup>3</sup>; polymerization in bulk; 333 K.  $M_2$ ,  $m_2$  is the content of MAA units in monomer blend and copolymer respectively. Here and in Fig. 7, I, II regions of homophase and heterophase copolymerization determined from light transmission.

FIG. 7. Curves of the composition of the copolymer AN-styrene obtained in presence of [DCC]=5 (1) and 200 (2) mole/m<sup>3</sup>; 313 K.  $M_2$ ,  $m_2$  is the content of AN units in the monomer blend and copolymer respectively.

It is important to note the fact that for the system styrene-MMA on polymerization in bulk M has no effect on the composition of the copolymer but it may be induced by worsening the dissolving capacity of the reaction medium. On adding a small amount of precipitant—cyclohexane, but with maintenance of the homogeneous character of copolymerization we also observed concerted change in the composition and  $[\eta]$  of the copolymer with change in the concentration of the initiator [11].

From all this it may be concluded that the effect of the dependence of the composi-

tion of the copolymer on  $M$  is manifest, in particular, in the dependence of the "instant" composition or the copolymerization constants on the concentration of radical initiator is characteristic of a considerable (if not predominant) number of systems of homogeneous radical copolymerization. The question of the nature of this phenomenon is still open and at present one may only formulate some propositions by way of preliminary conclusions.

TABLE 4. VALUES OF THE RELATIVE ACTIVITIES OF MONOMERS

$M_1$	$M_2$	Initiator	$c_{in}$ , mole/m <sup>3</sup>	$r_1$	$r_2$	$T$ , K	Nature of process
Styrene	MAA	DAA	12	$0.16 \pm 0.02$	$0.62 \pm 0.03$	333	Heterogeneous for MAA > 0.7
			200	$0.13 \pm 0.01$	$0.21 \pm 0.01$		
	MAA	BP	5	0.17	0.85	333	Ditto
			200	0.23	0.35		
	VA	BP	5	57.80	0.08	353	Homogeneous
			200	16.80	0.44		
	AN	CPC	5	0.35	0.01	313	Heterogeneous for AN > 0.9
			200	0.48	0		
	VDC	BP	5	1.81	0.15	333	Homogeneous
			200	2.17	0.13		
VA	VDC	BP	5	$0.12 \pm 0.09$	$4.70 \pm 0.90$	333	Heterogeneous for VDC > 0.4
			200	$0.07 \pm 0.06$	$3.60 \pm 0.70$		
	VP	BP	12	$0.11 \pm 0.11$	$9.00 \pm 0.67$	333	Homogeneous
			200	0.32	$4.80 \pm 0.10$		
		DAA	12	0.01	$11.2 \pm 0.40$		
			200	0.47	$2.90 \pm 1.30$		

As noted earlier, apparently the phenomenon described is due to factors of a physical nature of which the most probable is the selective sorption of the monomers by the polymer coils. The monomers as components of a mixed solvent have a different thermodynamic affinity for the copolymer. Regarding the coils of the latter as an osmotic cell one may expect that the monomer which is the best solvent will accumulate in it in large amount. Selective sorption of the monomers may lead to a difference in their effective concentration in the zone of the growth reaction from that set. Evidently, the effect depends on the density of the units in the coil growing with increase in it. In turn, the mean density of the units in the coil is inversely proportional to the square root of its  $M$ . Thus, we arrive at a possible theoretical validation of the observed relation between the composition and  $M$  of copolymers.

It should be noted that the ideas put forward help to explain the role of the precipitant on copolymerization of MMA-styrene [11]. Addition of precipitant causes compression of the polymer coils as a result of which the contribution of the effect of selective sorption to the effective concentration of the monomers becomes appreciable and leads to the appearance of the dependence of the composition on  $M$  of the copolymer.

*Translated by A. CROZY*



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Polymer Science U.S.S.R. Vol. 26, No. 4, pp. 788-794, 1984  
 Printed in Poland

0032-3950/84 \$10.00+.00  
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## EXPERIMENTAL INVESTIGATION OF THE PHASE DIAGRAMS OF CONCENTRATED SOLUTIONS OF RIGID-CHAIN POLYMERS WITH VARIOUS RIGIDITIES\*

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(Received 17 July 1982)

The conditions for forming lyotropic liquid-crystal order in mixed solutions of polymers having different values of geometrical asymmetry have been studied experimentally. It has been shown that the equilibrium composition of the phases depends essentially on the difference in the asymmetry of the components being mixed.

\* *Vysokomol. soyed.* **A26**: No. 4, 711-715, 1984.