

5. A. V. OBOLENSKAYA, V. P. SHCHEGOLEV, E. L. AKIM, N. L. KOSOVICH and I. Z. YEMEL'YANOVA, *Praktich. raboty po khimii drevesiny i tsellyulozy* (Practical Work on Wood and Cellulose Chemistry), p. 365, Lesn. promyshlennost', 1965
6. Z. I. KUZNETSOVA and V. S. IVANOVA, *Vysokomol. soyed.* **A9**: 1930, 1967 (Translated in *Polymer Sci. U.S.S.R.* **9**: 9, 2177, 1967)
7. A. I. POLYAKOV and L. N. SPIRIDONOVA, *Izv. Akad. Nauk SSSR, Otd. khim. n.*, **7**, 1562, 1969
8. G. E. MURREY and C. B. PURVES, *Canad. J. Chem.* **62**: 3194, 1940
9. G. H. SEGALL and C. B. PURVES, *Canad. J. Chem.* **30**: 860, 1952
10. L. J. TANGHE, L. B. GENUNG and J. W. MEZCH, In: *Whistler. Methods in Carbohydrate Chemistry*, Acad. Press, N.Y.-L., 1963
11. E. J. ROBERTS and S. P. ROWLANDS, *Carbohydr. Res.* **5**: 1, 1967
12. C. P. WADE, E. J. ROBERTS and S. P. ROWLAND, *J. Polymer Sci.* **B6**: 673, 1968

Polymer Science U.S.S.R. Vol. 25, No. 9, pp. 2151-2160, 1983
 Printed in Poland

0032-3950/83 \$10.00+.00
 © 1984 Pergamon Press Ltd.

SYNTHESIS OF ALTERNATING AND RANDOM COPOLYMERS OF ETHYLENE WITH MALEIC ANHYDRIDE*

R. A. TERTERYAN and V. S. KHRAPOV

All-Union Petroleum Processing Research Institute

(Received 4 March 1982)

The radical copolymerization of ethylene with maleic anhydride has been investigated over a wide range of pressure (10–150 MPa), temperature (70–235°) and comonomer concentrations (0.1–60 mole %) in the presence of various solvents and initiators. Only alternating copolymers are formed at 150°, irrespective of the initial ratio of monomers and pressure, and irrespective of the medium. Above 200° random copolymers containing 0.4–13 mole% anhydride units are formed. The relative reactivity of ethylene in the random copolymerization was equal to 0.045 ± 0.019 . The dependence of the rate of formation of alternating copolymers on the maleic anhydride concentration was expressed by an extremal type of relationship, a maximum being obtained at an equimolar ratio of monomers. It was found that the rate and degree of copolymerization depend on pressure and temperature, on the polarity of the solvent, and on the initiator concentration.

INVESTIGATORS have long been investigating the radical copolymerization of various monomers with maleic anhydride (MA). This is because MA, being a difficultly polymerizable monomer, enters readily into copolymerization reactions

* *Vysokomol. soyed.* **A25**: No. 9, 1850–1857, 1983.

and forms high polymers that are normally of equimolar composition, and have an alternating distribution of monomer units [1-5]. In contradistinction to the fully investigated systems of MA copolymerization with monomers such as styrene [1] and vinyl acetate [5], little study appears to have been made of the synthesis of ethylene-MA copolymers: two papers published in [6, 7] relate only to low pressures (up to 4 MPa) and to temperatures (up to 70°), whereupon only alternating copolymers were obtained.

In view of the practical importance of processes of free-radical copolymerization of ethylene, it seemed appropriate to investigate the synthesis of ethylene-MA copolymers over a wide range of pressure, temperature and other conditions, to ascertain whether not only alternating but also statistical copolymers of these monomers, containing less than 50 mole% anhydride groups, could be prepared.

Copolymerization experiments were carried out, using both batch and continuous action laboratory apparatus, under pressures of up to 150 MPa. The operation of the batch action autoclave apparatus and the experimental procedure in the synthesis of the copolymers were as described in [8]. The continuous process of ethylene-MA copolymerization was conducted in a circulatory type reactor with stirrer (1500 rev/min); this 0.8 l. reactor was equipped with a thermostatted jacket.

MA of analytical purity (99.9% basic substance) was used; the solvents—benzene, toluene, acetone, DMF, cyclohexanone (CH), methyl ethyl ketone (MEK) and acetonitrile were of chemically and analytically pure grades. The ethylene composition was the same as in [8]. Azoisodibutyronitrile (ABN) was thrice reprecipitated from solution in acetone, and then vacuum dried at room temperature, m.p. 103°; tertiary butyl peroxide (TBP) contained not less than 95% of the basic substance.

Unreacted reagents were removed from the copolymerization products by reprecipitation in appropriate solvents selected according to the type of copolymer (for alternating copolymers, reprecipitation with benzene from solution in acetone, for statistical copolymers reprecipitation with acetone from solution in benzene), after which the copolymers were vacuum dried to constant weight.

Copolymer compositions were determined by elemental analysis and by the hydrolysis method, and were found to be in satisfactory agreement. Estimates of MW were obtained for the alternating copolymers in line with the equation [7]

$$[\eta]_{\text{DMF}}^{25} = 2 \times 10^{-3} M_w^{0.5},$$

where $[\eta]_{\text{DMF}}^{25}$ is the intrinsic viscosity, at 25°, of a solution of the copolymer in DMF with an LiCl solution, concentration 0.1 mole/l. added. The melt flow index was determined at 125° for the statistical copolymers, load 125 g, nozzle diameter 1.18 mm.

It is clear from the data in Tables 1 and 2 regarding the composition of the copolymers obtained by batch polymerization that, irrespective of the MA concentration in the monomer mixture (varying over the range 0.1-60 mole%) under 10-150 MPa pressure, temperature 70-150°, only copolymers of equimolar composition are obtained. This is the case both in the bulk copolymerization processes (Table 1), and when the reaction is run in various solvents, particularly in benzene, in which the monomers dissolve, but ethylene-MA copolymers do not, and in CH, which is a good solvent for all components of the reaction mixture

TABLE 1. BULK COPOLYMERIZATION OF ETHYLENE WITH MA AT 100 MPa, TEMP. 70°

M_2^0 , mole %	M_2^{end} , mole %	Time, hr	Conversion, %			m_2 , mole%
			total	in respect to ethylene	in respect to MA	
[ABN]=0.0005 mole/l. (0.0027 mole%)						
0.47	0.25	2	1.0	0.2	46	47.0
2.48	1.94	3	1.9	0.5	19	—
2.86	2.72	1	0.6	0.1	5	50.6
4.28	3.44	4	3.6	0.9	21	49.1
[ABN]=0.0012 mole/l. (0.0066 mole%)						
0.95	0.22	4	3.2	0.7	78	46.7
2.86	1.23	4	6.8	1.7	57	53.0
5.70	3.43	3	9.7	2.6	43	50.0
8.23	5.56	2.5	11.2	3.3	36	52.1
9.50	4.96	4	18.2	5.5	53	48.9
[ABN]=0.0020 mole/l. (0.0110 mole%)						
1.81	1.07	4	3.3	0.8	42	49.7
3.60	2.85	4	3.3	0.9	21	46.1
5.40	4.41	3	4.7	1.2	21	48.0
5.50	4.46	2	5.3	1.5	23	48.5
5.60	4.15	4	6.0	1.4	28	51.6
9.30	8.30	4	5.6	2.3	16	46.7

Note. Here and below M_2^0 and M_2^{end} are the initial and the end concentrations of MA in the monomer mixture; m_2 is the amount of MA units in the copolymer.

(Table 2). Thus a change from a heterogeneous copolymerization system to a homogeneous one does not affect the composition of the resulting copolymers.

In view of the experimental results we surmise that under the conditions adopted ethylene-MA copolymerization, like most systems for copolymerization of MA, takes place by a donor-acceptor mechanism, involving formation of an equimolar electron donor acceptor charge-transfer complex (CTC) between ethylene and MA followed by its homopolymerization. Let us consider the method of synthesis from the standpoint of complex formation between ethylene and MA. As the pressure rises, it is to be expected that the equilibrium complexation constant will increase, since the molar volume of the complex is, apparently, less than the sum of the molar volumes of the starting materials. It follows that the pressure need not influence the alternating copolymer composition, since it tends to increase the amount of CTCs in the system. This assumption is borne out by the data in Table 2.

One of the factors influencing donor-acceptor copolymerization is the presence of polar solvents [9-12], since the CTC stability constant decreases as the dielectric constant rises. In view of this ethylene-MA copolymerization experiments were

TABLE 2. COPOLYMERIZATION OF ETHYLENE WITH MA IN A MEDIUM OF BENZENE AND CYCLOHEXANONE

M_2^0 , mole%	M_2^{end} , mole%	Time, hr	Conversion, %			m_2 , mole %
			total	in respect to ethylene	in respect to MA	
$p=150$ MPa, $T=70^\circ$, [benzene]=3.6 mole/l. (21.4 mole%), [ABN]=0.0012 mole/l. (0.0084 mole/%)						
0.61	0.12	1.7	2.2	0.5	83	47.5
1.9	0.80	1.0	4.6	1.2	63	47.1
3.8	1.4	1.0	10.0	2.5	65	50.5
8.9	3.9	1.0	21.2	6.4	64	51.0
$p=100$ MPa, $T=130^\circ$, [benzene]=3.6 mole/l. (22.6 mole%) [TBP]=0.00088 mole/l. (0.0073 mole/%)						
1.5	1.1	1.0	1.7	0.4	26	52.3
3.8	2.7	1.0	4.9	1.3	31	51.0
8.2	6.3	1.0	8.6	2.5	28	47.5
8.2	4.2	2.0	16.6	4.8	54	48.1
15.6	13.2	1.0	10.2	3.7	20	50.1
23.6	21.0	1.0	13.1	6.0	20	53.0
$p=10$ MPa, $T=130^\circ$, [CH]=2.3 mole/l. (36.0 mole%) [TBP]=0.033 mole/l. (0.82 mole/%)						
16.6	5.0	2.0	41.0	15.3	78	50.0
25.4	1.9	2.0	62.0	33.0	96	52.1
36.0	27.2	1.0	44.0	29.0	52	48.7
39.5	37.3	1.0	47.0	37.0	51	49.1
52.5	53.6	1.0	36.3	36.9	36	50.7
56.0	62.0	2.0	50.0	59.0	48	50.6

carried out, using various solvents that form complexes with MA. However, it appears from the data in Table 3 that the polarity of the solvent does not influence the copolymer compositions. This is apparently attributable to inadequate reactivity of MA-solvent complexes in copolymerization reactions with ethylene. Certainly, in the case of strongly polar solvents such as DMF and acetonitrile it may well be that such solvents bind all the MA in stable complexes, thereby suppressing the process.

It is very interesting to consider the influence of temperature in donor-acceptor copolymerization processes. Investigations recently reported in [13-15] show that a rise in temperature makes for diminution of the alternating tendency up to the point where statistical copolymers are formed. It was found that for the system MA-styrene cessation of complexation (and thus cessation of formation of statistical copolymers) appears at temperatures above 130° [14], while for the MA-vinyl acetate system it appears at a temperature above 90° [15].

TABLE 3. INFLUENCE OF POLARITY OF THE SOLVENT ON THE COPOLYMERIZATION OF ETHYLENE WITH MA

$[MA]=0.49$ mole/l., $M_2^0=4.8$ mole%, $[solvent]=3.6$ mole/l. (27 mole%), $[ABN]=0.0025$ mole/l. (0.025 mole%), time 1 hr, 40 MPa, 70°

Solvents	Dielectric constants of solvents at 25°	Equilibrium constant of MA-solvent complex formation[12]	m_2 , mole%	w , mole/l.·hr	$\bar{M}_w \times 10^{-3}$
—	—	—	50.5	0.27	55
Toluene	2.1	—	49.1	0.79	29
Benzene	2.3	0.16	51.0	0.74	36
Ethyl acetate	6.0	—	48.7	0.68	100
MEK	18.5	0.31	51.4	0.52	90
CH	19.0	—	50.6	0.79	8
Acetone	22.5	0.67	50.2	0.34	20
DMF	36.7	—	—	0	—
Acetonitrile	37.5	—	49.5	0.06	2

TABLE 4. STATISTICAL COPOLYMERIZATION OF ETHYLENE WITH MA IN THE CONTINUOUS ACTION APPARATUS

(Time spent in the reaction zone 4.7–5.7 min; 235°)

M ₂ , mole%	p, MPa	[CH], mole%	[TBP], mole%	Conversion, %			m ₂			Copolymer density, g/cm ³	T _{mp} ^o	MFI*, g/10 m
				total	with respect to ethylene	with respect to MA	hydrolysis method, wt. %	based on elemental analysis				
								wt. %	mole %			
0	141	1.1	0.0004	21	21	—	0	0	1.933	0.933	105	14
0.07	140	1.1	0.0004	20	19	55	2.2	2.2	0.6	0.938	103	23
1.16	75	1.1	0.0004	14	14	25	—	1.4	1.4	—	103	245
0.14	140	1.1	0.0004	8	7	62	11.0	10.3	3.2	0.958	98	41
0.06	140	1.1	0.0025	18	17	90	6.8	6.6	2.3	—	100	140
0.10	190	1.1	0.0025	12	11	76	8.1	8.4	2.6	—	—	180
0.26	75	1.1	0.0150	8	7	34	5.8	5.7	1.7	0.946	101	358
0	140	3.0	0.0004	11	11	—	0	0	0	0.937	105	240
0.14	140	3.0	0.0004	6	5	60	11.4	13.2	4.1	0.965	95	39
0.46	140	3.0	0.0004	6	4	43	—	24.0	8.2	0.989	90	17
0.88	140	3.0	0.0004	3	2	25	—	31.0	13.0	—	82	6

* MFI—melt flow index,

In the process of batch copolymerization of ethylene with MA a temperature rise up to 150°, even in the case of low MA concentrations in the monomer system, does not lead to any departure from an equimolar copolymer composition. Apparently, this means that, under high pressure conditions, the ethylene-MA complex is more stable than complexes formed in the foregoing systems.

In earlier work [16] we found that ethylene-MA statistical copolymers are formed at temperatures above 200°. The copolymers obtained at an MA concentration of up to 1 mole % in the monomer system contained from 0.4 to 13 mole % MA units (Table 4). Evidence that the copolymers are obtained, not a mixture of PE with copolymer containing an equimolar amount of the comonomers) is provided by the solubility data for the copolymers and by the results of their fractionation by fractional dissolution in the system xylene-monoethyl ether of ethylene glycol. For instance fraction of the copolymer containing 3.1 mole % MA was unaccompanied by formation of homopolymers, and the number of MA units in the fractions varied from 2.9 to 4.1 mole %.

On the basis of the composition of the statistical copolymers we found that the relative reactivity of ethylene in the copolymerization with MA at 140 MPa and 235° $r=90.045 \pm 0.019$ and $r^2=0$. Figure 1 shows the dependence of the copolymer composition on that of the monomer mixture calculated from these constants. The curve is in good agreement with the experimental results.

Definite differences appear if one studies the influence of monomer conversion in the synthesis of the alternating and statistical copolymers. Tables 1, 2 and 4 give the results of the total conversion (based on the total mass of the monomers) and in regard to the two monomers individually. It can be seen that in all cases the conversion of MA significantly exceeds (in some cases by 1-2 orders) that of ethylene. This difference in monomer conversions leads to a marked change in the ratio of monomers in the reaction system, though in contradistinction to the statistical copolymerization, where this change involves a consequent change in the copolymer composition, the copolymer composition remains equimolar in the formation of alternating copolymers. This is one of the good features of the process, since a product of homogeneous composition is obtained irrespective of the monomer ratio and the conversion of monomers.

It is worthwhile making a comparative kinetic study of the synthesis of the alternating and statistical copolymers. In the case of the alternating copolymerization investigated over a wide range of change in the MA concentrations it was found that the reaction rate bears an extremal character (Fig. 2), the maximum appearing at an equimolar ratio of monomers in the reaction system, where it is also be expected that the CTC concentration will be highest. This is typical for donor-acceptor copolymerization processes [3], though deviations do occur, particularly displacement of the maximum [5]. In view of this the results reported in [7] merit special attention, as these are at variance with our findings since those authors [7] on varying the MA concentration in the mixture with ethylene from 30 to 80 mole % did not find that plots of the copolymerization rate bear an extremal

character. This led them to suppose that the process taking place in this case was alternating copolymerization with a limiting step, ethylene addition to terminal MA. It appears that those authors neglected two factors: firstly, that the total molar concentration of monomers is reduced (from 3.4 to 1.2 mole/l.) as the MA concentration increases within the foregoing interval, which could not fail to have an effect on reduction in the reaction rate, and, secondly, data are lacking in regard to the reaction rate when the MA concentration is less than 30 mole %.

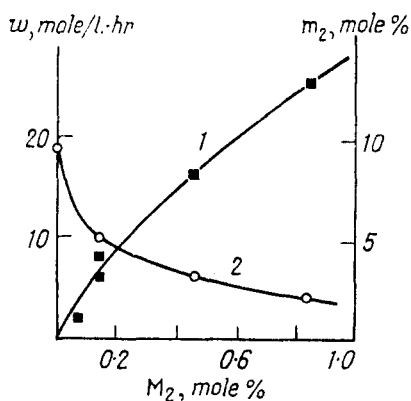


FIG. 1

FIG. 1. Composition (*I*) of statistical ethylene-MA copolymers and the copolymerization rate vs. MA concentration in the monomer mixture (M_2) under conditions of continuous copolymerization at 140 MPa and 230°. [TBP]=0.0004 mole %, [CH]=3 mole %, time spent in the reaction zone, 5-7 min.

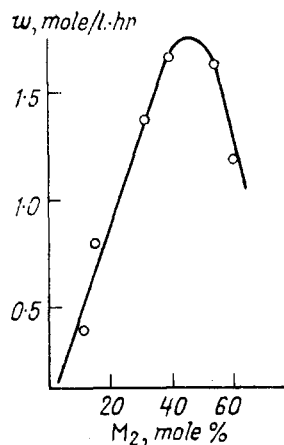


FIG. 2

FIG. 2. Rate of alternating copolymerization of ethylene with MA vs. MA concentration in the monomers at 10 MPa, 130°, [TBP]=0.82 mole %, [CH]=36.0 mole %.

It seems to us that though direct proof of the ethylene-MA CTC may be lacking (in view of experimental difficulties in identifying the latter under high pressure conditions), the sum total of the indirect facts outlined above suggests that copolymerization under the conditions in question takes place via a mechanism of CTC formation.

The curves in Fig. 3 show the rate of formation of alternating copolymers at low MA concentrations (up to 10 mole %) under various conditions in regard to pressure, temperature, initiator concentration and the medium used. It is seen from the Figure that, on going from bulk copolymerization (curve 4) to the reaction in benzene medium (curve 2), other conditions being identical, there is a more marked increase in the reaction rate, which is accounted for by homogenization of the monomer mixture leading to a higher concentration of the ethylene-MA complex. At 70° we have in all cases (curves 1, 2, 4, 5) linear relations between

the reaction rate and the MA concentration in the monomer mixture. Here it should be noted that, in the absence of MA, no polymer is formed under the stated conditions. In other words, the alternating polymerization is taking place actively under conditions whereby not one of the monomers polymerizes separately. It follows from this that the reactivity of the ethylene-MA complex must be high.

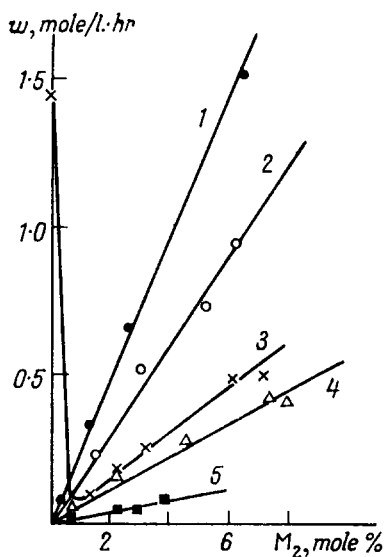


FIG. 3

FIG. 3. Influence of low concentrations of MA on the rate of copolymerization in benzene medium (1-3) and in bulk (4, 5): 150 (1) and 100 MPa (2-5); 70 (1, 2, 4, 5) and 130° (3); [ABN]=0.0012 (1, 2, 4) and 0.0005 mole/l., (5). [TBP]=0.0088 mole/l. (3).

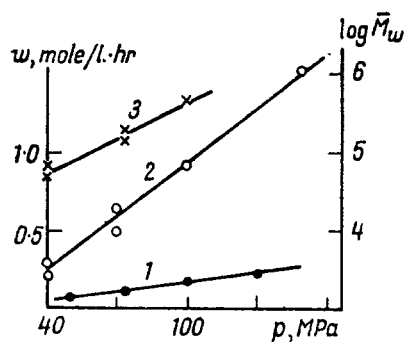


FIG. 4

FIG. 4. Rate of alternating copolymerization (1, 2) and MW of the ethylene-MA copolymers (3) vs. pressure (at 70°, [ABN]=0.00012 mole/l.): 1—in bulk, $M_2=2$ mole %; 2, 3—[benzene]=3.6 mole/l. $M_2=6.7$ mole %.

A slightly different pattern is observed at 130° (Fig. 3, curve 3). The homopolymerization rate of ethylene in this case exceeds the copolymerization rate, a fact that is attributable to a regular reduction in the equilibrium complexation constant leading to a lower number of CTC in the system, and reducing the reaction rate accordingly. This is why the introduction of MA leads to a sharp reduction in the reaction rate, and, when the MA concentration is thereafter increased, to a corresponding linear increase in the rate. Accordingly, when the temperature rises, the alternating polymerization rate, in contradistinction to the normal power law, is reduced.

Finally, a completely different pattern of change in the reaction rate appears when the process is conducted at temperatures above 200° (Fig. 1). Here we have a

statistical copolymerization process. In this case the reaction rate falls monotonically as the MA concentration is increased: apparently this is the result of a higher rate of cross termination compared with the elementary propagation steps. An increase in the CH concentration in the reaction system tends to reduce the rate (Fig. 1) and degree of polymerization (judging by values of the melt flow index given in Table 4).

As the dielectric constant of the solvent increases, the rate of formation of alternating ethylene-MA copolymer is generally reduced (Table 3), which accords with conclusions reported in [10].

In the synthesis of both the alternating (Fig. 4) and the statistical copolymers (Table 4) a pressure rise is reflected in a regular increase in both the rate and degree of copolymerization.

A study of the influence of the initiator concentration revealed clear differences in the effect of the latter on the synthesis of the alternating and statistical copolymers. In all cases examined it was found that no copolymer is formed in the absence of the initiator. The rate and the degree of copolymerization increase very significantly (Fig. 5) on increasing the TBP concentration in the synthesis of alternating copolymers in benzene medium: in this case the order of the reaction rate with respect to TBP is 1.6. Such a high value for the order of the rate with respect to initiator apparently stems from heterogeneity of the monomer mixture-polymer system, since polymer, in the case in question, is a solid product that is insoluble in the reaction medium.

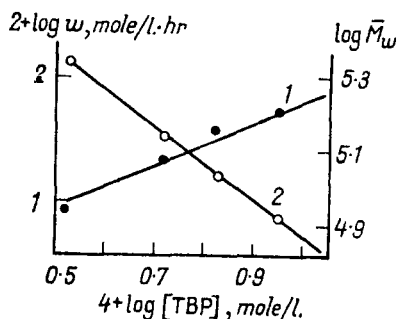


FIG. 5. Influence of the TBP concentration on the rate (1) of copolymerization of ethylene with MA and MW of the product (2) at 100 MPa, 130°, [benzene]=3.6 mole/l., $M_2=6-7$ mole %.

A study of the statistical copolymerization at 140 MPa, 235° and [TBP] = 0.002–0.016 mole % shows that the order of the reaction rate with respect to initiator is 0.45, which is close to the theoretical value of 0.5 for the free-radical polymerization.

Let us turn, in conclusion, to properties of the synthesized copolymers. The alternating copolymers are solid thermosetting products having a decomposition

temperature of 220° and density 1.390 g/cm³ (at 25°) irrespective of MW; the copolymers dissolve readily in polar solvents such as acetone, MEK, CH and DMF, and are insoluble in aromatic and aliphatic hydrocarbons. It appears from the results of electron microscopy and X-ray analysis [17] that the copolymers are amorphous, despite the regularity and homogeneity of their molecular structure.

In contradistinction to the alternating copolymers, the properties of the statistical ones are close to those of low density PE. The statistical copolymers are solid thermoplastic products that dissolve in aromatic hydrocarbons, and are insoluble in polar solvents. The melting point falls as the number of MA units in the copolymers increases, and at the same time their density is increased (Table 4).

Translated by R. J. A. HENDRY

REFERENCES

1. E. TSUCHIDA, J. Chem. Soc. Japan, Industr. Chem. Sec. **70**: 4, 573, 1937
2. P. S. SHANTAROVICH, L. N. SOSNOVSKAYA and T. P. POZHANOVA, Dokl. Akad. Nauk SSSR **191**: 1, 100, 1970
3. Z. M. RZAEV, Z. V. BRYKSINA and S. I. SADYKH-ZADE, J. Polymer Sci., Polymer Symp., **42**, 519, 1973
4. M. RÄTZSCH and J. SCHICHT, Acta Polymerica **31**: 7, 413, 1980
5. C. CAZE and C. LOUCHEAUX, J. Macromolec. Sci. **A9**: 1, 29, 1975
6. M. SUCO, S. TAKASHI, J. MASAO and K. TSUTOMU, J. Polymer Sci. A-1, **4**: 4, 821, 1966
7. A. S. SEMENOVA, M. I. LEITMAN, L. G. STEFANOVICH and L. F. SHALAYEVA, Vysokomol. soyed. **A14**: 2102, 1972 (Translated in Polymer Sci. U.S.S.R. **14**: 10, 2470, 1972)
8. R. A. TERTERYAN, Yu. I. BARASH and L. N. SHAPKINA, Vysokomol. soyed. **10**: 1673, 1968 (Translated in Polymer Sci. U.S.S.R. **10**: 7, 1940, 1968)
9. E. TSUCHIDA, T. TOMONO and H. SANO, J. Chem. Soc. Japan, Industr. Chem. Sec. **74**: 6, 1203, 1971
10. A. N. PRAVEDNIKOV and S. N. NOVIKOV, Preprints Int. Symp. Macromolec., Helsinki, **2**: 1, 727, 1972
11. M. RÄTZSCH, Plaste und Kautschuk **19**: 3, 169, 1972
12. E. TSUCHIDA, T. TOMONO and H. SANO, Macromolec. Chem. **151**: 245, 1972
13. R. B. SEYMOUR and D. P. JARNER, Polymer News **4**: 5, 209, 1978
14. R. B. SEYMOUR and D. P. JARNER, J. Paint. Technol. **48**: 612, 41, 1976
15. R. B. SEYMOUR, D. P. JARNER and L. J. SOMDERS, J. Macromolec. Sci. **A13**: 2, 173, 1979
16. R. A. TERTERYAN, V. S. KHRAPOV, I. M. PERVUSHINA, A. P. GOLOSOV and V. I. MONASTYRSKII, U.S.S.R. Pat. 572470, Byull. izobret., **34**, 56, 1977
17. R. A. TERTERYAN, M. B. KONSTANTINOPOL'SKAYA, Z. Ya. BERESTNEVA and V. A. KARGIN, Vysokomol. soyed. **A11**: 2585, 1969 (Translated in Polymer Sci. U.S.S.R. **11**: 11, 2940, 1969)