THE INFLUENCE OF MONOMER STRUCTURE ON POLYPROPYLENE MODIFICATION IN EMULSION

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Dedicated to the Academician O. Wichterle on the occasion of his 70th birthday.

Oxidized isotactic polypropylene powder is chemically modified by monomers of widely differing structure, the reaction being carried out at 30°C in aqueous emulsion in the presence of a ferrous chelate as an activator. Apart from the polymer bonded to the polypropylene carrier also some homopolymer is formed simultaneously during this heterogeneous polymerization initiated by polypropylene peroxides. The mutual proportion and amount of the resulting polymers may be considerably influenced by the properties of the monomer used, such as by its partial or total solubility in water, its polarity and reactivity as well as by the substituent size. Moreover, the chelate and emulsifier type as well as the presence of organic liquid phase in the system play also an important role. The mechanistic discussion is focused to the early initiation stage of the polymerization. This period, together with the active participation of the monomer, is decisive for the formation of both polymer types produced in the system. The results obtained are in accordance with the observed heterogeneous distribution of —O—O— groups in oxidized polypropylene.

The polymerization that is initiated by isotactic polypropylene peroxides at 30°C in the presence of an emulsifier is influenced both by the chelate activator[1] of initiator and emulsifier[2,3] as well as by the heterogeneous polyperoxide[4]. The choice of the type and concentration of these components determines the final yield and proportion of the resulting polymers *i.e.* homopolymer and polymer as side chains of polypropylene (in the following text these side-chains are called bonded polymer only). As noticed before[5,6], another important component determining the yield and character of the resulting polymer is the monomer. It is thus a purpose of this work to examine the effect of monomer in the polymerization system taking into account also other components, namely the emulsifier and activator. Four monomers with a limited water solubility have been examined (styrene, α-methylstyrene, methyl acrylate and methyl methacrylate) as well as four monomers soluble in water (acrylic acid, methacrylic acid, acrylamide and methacrylamide). This monomer series was further complemented by homologues of acrylic and methacrylic esters which differ very little from the structural point of view.

EXPERIMENTAL

Chemicals

Isotactic polypropylene powder, ferrous sulphate ($FeSO_4.7\,H_2O$), chelating agents, such as 1,8-diamino-3,6-diazaoctane and disodium ethylenediaminetetraacetic acid have been described previously[5]. Emulsifiers, such as Mersol H ,($CH_3—(CH_2)_{16}—SO_3Na$), produced by Leuna Werke, GDR and Slovasol 2430, ($CH_3—(CH_2)_{23}—(CH_2—CH_2—O)_{29}—C_2H_4OH$), made by CHZWP Nováky, were the commercial products. The monomers, such as styrene. α-methylstyrene, acrylic acid, methacrylic acid, acrylamide, methacrylamide and methyl methacrylate were purified by a partial polymerization followed by distillation *in vacuo* or by recrystallization. Acrylic esters, *i.e.* methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate and pentyl acrylate were prepared by the esterification of acrylic acid by a twofold molar excess of a corresponding alcohol, *p*-toluenesulphonic acid (0·4 mol.%) being present as a catalyst. Ethyl methacrylate, propyl methacrylate, butyl methacrylate and pentyl methacrylate were prepared in the same system by the re-esterification of methyl methacrylate by corresponding alcohols. The esters were washed with water, dried over $CaCl_2$ and rectified in a nitrogen atmosphere. Other organic solvents and nitrogen were of analytical grade.

Procedures and Apparatus

Isotactic polypropylene (PP) powder was fluid oxidized at a room temperature for 60 minutes, by oxygen containing ozone ($12\ \text{mg}\ \text{l}^{-1}$). After the oxidation, the polypropylene contained hydroperoxide ($15\ \text{mmol}\ \text{kg}^{-1}$) and a more stable polypropylene peroxide ($22\ \text{mmol}\ \text{kg}^{-1}$)[7].

The polymerization was carried out at 30°C under nitrogen in rotating ampoules[8]. The typical polymerization system contained the solid phase, represented by 0·35 g of oxidized PP, and 5 ml of the liquid phase containing water, the monomer ($0{\cdot}7\ \text{mol}\ \text{l}^{-1}$), the emulsifier ($8{\cdot}8\ \text{mmol}\ \text{l}^{-1}$), and the activator ($2{\cdot}4\ \text{mmol}\ \text{l}^{-1}$). The latter consisted of $FeSO_4$–1,8-diamino-3,6-diazaoctane (molar ratio 2 : 3) or $FeSO_4$–disodium ethylenediamine tetraacetic acid (molar ratio 1 : 1). The mole concentrations are expressed per liter of the liquid phase emulsion. In some cases the system contained also a water-insoluble liquid (30% v/v). This was effected on account of water, the total volume of liquid phase being preserved. After the end of polymerization run, the solid phase containing both unchanged and modified PP was separated by the filtration through a sintered glass disc. It was washed with water and with a solvent for homopolymer. After the final washing with acetone it was dried to constant weight. The homopolymer present in the filtrate emulsion was precipitated by adding a suitable precipitant. Unless otherwise stated, the polymerization yield was calculated separately for the bonded polymer and for the homopolymer. When the monomer concentration was changing in the system then the result of modification was expressed by characterizing the composition of the modified polypropylene, *i.e.* in % of bonded polymer present in the solid phase.

RESULTS AND DISCUSSION

When comparing the polymerization activity of various monomers, the composition of the polymerization system represents certain problems since some monomers, namely those which are water-soluble, require the presence of another, water-insoluble, component[6]. Thus all the studied monomers had to be examined under these conditions. For this reason, experiments were made in the presence of three different solvents[6] in order to assess their influence upon the modification of polypropylene (PP) by those monomers which do not require the presence of organic phase. Fig. 1 demonstrates the influence of these solvents on the modification by acrylic and methacrylic esters. When compared with the system without the solvent, the degree of modification is practically unchanged even when the system contained either benzene or hexane or ethyl acetate (curves *1*). When methacrylic esters were used (curves 2), the influence of solvents upon the PP modification becomes more pronounced. This indicates that in individual cases the presence of solvent may influence the result of modification.

The results presented in Table I, being in accordance with our previous observation[1], indicate that the presence of an organic, water-insoluble liquid preserves the apparent zero-order character of the polymerization reaction towards monomer although the polymerization yield is lowered. Quite a different situation is created when a component is added which, under certain conditions, makes the monomer soluble in water. Fig. 2 (curve *1*) shows such an example where the modification was carried out by methyl methacrylate in the presence of dimethylformamide as a solvent. In the concentration region where the monomer becomes totally dissolved in the system, this region being shifted towards lower concentrations of solvent as a consequence of the presence of emulsifier, the polymerization rate rapidly decreases. A similar phenomenon was observed when acrylonitrile was used without a solvent[1]. The effect was particularly pronounced at lower monomer concentrations than those corresponding to its solubility in water (Fig. 2, curve 2.) It may, therefore, be assumed that the rate of polymerization of a given monomer can be influenced by changing its solubility in the system being polymerized. The results shown in Fig. 1 seem to confirm this assumption.

Tables II and III summarize the results obtained during PP modification by eight monomers of a considerably different structure, using four types of polymerizaton systems containing different activators and emulsifiers. Moreover, the runs were carried out in the presence of three

TABLE I

The influence of a solvent upon the amount of bonded polymer in solid phase on the polymerization of styrene and methyl methacrylate (20 min) initiated by oxidized isotactic polypropylene

Monomer mol l^{-1}	Solvent	Bonded polymer %
Styrene, $FeSO_4$–1,8-diamino-3,6-diazaoctane, Mersol H		
0·7	—	22·9
2·1[a]	—	23·2
0·7	benzene	14·7
2·1[a]	benzene	15·0
Methyl methacrylate, $FeSO_4$–disodium ethylenediamine tetraacetic acid, Mersol H		
0·7	—	12·6
2·1[a]	—	12·2
0·7	ethyl acetate	6·4
2·1[a]	ethyl acetate	6·3

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[a] The increased concentration was effected on account of water volume.

types of water-insoluble liquids and compared with the runs where no solvent was added. The obtained results show the possibility of an efficient control of the polymerization direction by changing the type of certain components of the polymerization system. This concerns mainly monomers exhibiting a partial solubility in water (styrene, α-methylstyrene, methyl acrylate, and methyl methacrylate). So, *e.g.* in a system containing the $FeSO_4$–1,8-diamino-3,6-diazaoctane and the ionic emulsifier, Mersol H (Table III), the formation of bonded polymer predominates

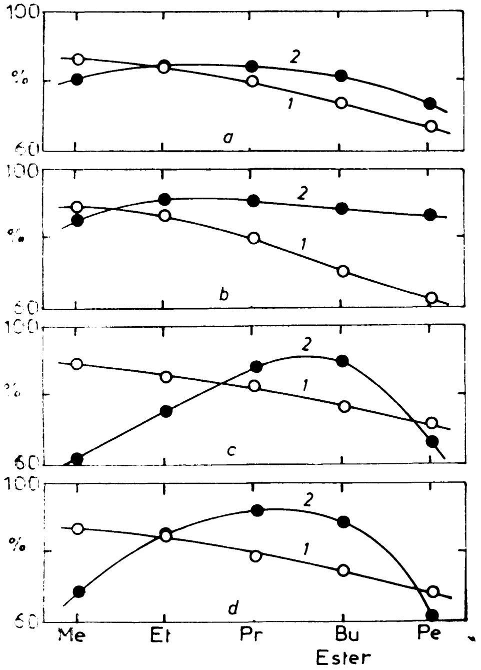

FIG. 1

The influence of ester group length in acrylic *1* and methacrylic *2* esters (activator $FeSO_4$-1,8-diamino-3,6-diazaoctane, emulsifier Mersol H, 6 h) in the presence of various solvents (30% v/v) on yield of bonded polymer. *a* without solvent, *b* benzene, *c* n-hexane, *d* ethyl acetate

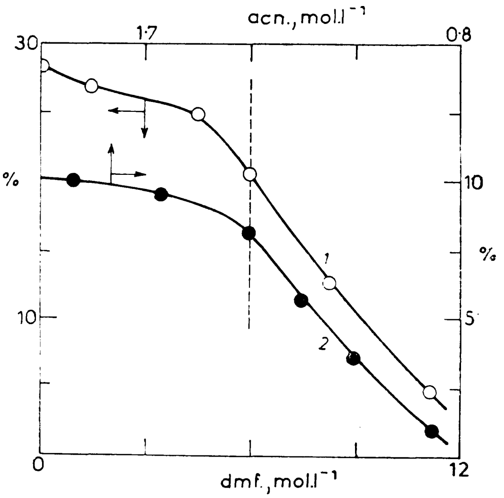

FIG. 2

The influence of dimethylformamide concentration ($mol\ l^{-1}$) in PP-modification by methyl methacrylate *1* and the influence of acrylonitrile concentration ($mol\ l^{-1}$) in PP-modification by acrylonitrile *2* upon the amount of bonded polymer in the solid phase (emulsifier Mersol H). Curve *1* activator $FeSO_4$–1,8-diamino-3,6-diazaoctane; polymerization time 20 min; curve *2* activator $FeSO_4$–disodium ethylenediamine-tetraacetic acid, 3 h. Broken line denotes the solubility region of both monomers in the system without the emulsifier (acn acrylonitrile, dmf dimethylformamide)

TABLE II

The influence of polymerization system composition upon the results of polymerization of various monomers. Activator $FeSO_4$–disodium ethylenediaminetetraacetic acid, polymerization time 6 h. Symbols: *e* average value of monomer polarity[9,10], *Q* general reactivity of monomer[9,10], *S* solubility of monomer in water at 30°C (ref.[11]); w.s. without solvent, acetate means ethyl acetate

Monomer	*e*	*Q*	*S*	Bonded polymer, %/Homopolymer, %							
				ionic emulsifier (Mersol H)				non-ionic emulsifier (Slovasol 2430)			
			%	w.s.	benzene	hexane	acetate	w.s.	benzene	hexane	acetate
Styrene	−0·80	1·00	0·03	5·5	0·8	0·0	12·3	5·5	0·2	0·0	0·4
				79·4	8·2	13·0	5·9	68·2	19·1	14·3	29·2
α-Methylstyrene	−1·27	0·98	0·06	0·1	0·0	0·0	0·0	0·1	0·0	0·0	0·0
				0·6	0·0	0·1	0·0	1·0	0·1	0·0	0·0
Methyl acrylate	0·60	0·42	5·2	60·0	43·5	67·1	66·3	3·6	2·0	1·2	1·9
				39·0	22·8	31·9	24·7	88·0	69·4	70·7	78·9
Methyl methacrylate	0·40	0·74	1·5	28·3	22·2	28·3	55·9	10·5	0·7	2·7	3·7
				61·5	21·2	26·6	22·3	72·8	32·7	22·2	49·3
Acrylic acid	0·77	1·15			44·5	28·3	26·7		24·3	4·2	11·6
					2·1	2·5	3·3		7·6	5·2	4·6
Methacrylic acid	0·65	2·34			94·6	93·2	88·3		72·4	82·9	44·9
					4·4	5·8	10·7		26·6	16·1	6·6
Acrylamide	1·19	1·12			39·7	35·7	33·9		10·5	2·0	72·7
					6·8	9·0	8·1		6·6	6·8	5·8
Methacrylamide	1·24	1·46			48·9	49·2	89·0		1·8	0·5	10·8
					3·7	6·9	10·0		1·6	3·5	1·7

TABLE III

The influence of polymerization system composition upon the results of polymerization of various monomers. Activator $FeSO_4$–1,8-diamino--3,6-diazaoctane, polymerization time 6 h. Symbols: e average value of monomer polarity[9,10], Q general reactivity of monomer[9,10], S solubility of monomer in water at 30°C (ref.[11]); w.s. without solvent, acetate means ethyl acetate

Monomer	e	Q	S	Bonded polymer, %/Homopolymer, %							
				ionic emulsifier (Mersol H)				non-ionic emulsifier (Slovasol 2430)			
			%	w.s.	benzene	hexane	acetate	w.s.	benzene	hexane	acetate
Styrene	−0·80	1·00	0·03	80·9	67·8	53·5	47·3	14·6	8·8	2·6	3·6
				6·8	1·6	2·4	1·7	25·7	4·6	2·0	2·5
α-Methylstyrene	−1·27	0·98	0·06	9·7	0·5	0·4	0·9	1·0	0·1	0·1	0·0
				0·6	0·2	0·2	1·3	0·6	0·4	0·6	0·5
Methyl acrylate	0·60	0·42	5·2	86·1	89·4	89·0	87·3	49·6	31·0	33·1	33·0
				12·9	9·6	7·5	11·5	32·8	30·5	20·3	39·1
Methyl methacrylate	0·40	0·74	1·5	82·0	85·1	60·7	69·5	46·9	27·2	21·3	15·5
				4·3	2·9	3·9	3·1	25·8	9·5	11·9	7·3
Acrylamide	1·19	1·12			43·7	49·6	49·7		69·2	54·7	93·0
					5·4	5·4	3·7		8·7	9·9	5·5
Methacrylamide	1·24	1·46			29·7	45·2	54·1		87·5	73·9	87·1
					2·4	3·6	2·7		11·5	11·0	11·9

over the formation of homopolymer. On the other hand, the system $FeSO_4$–disodium ethylenediaminetetraacetic acid and the non-ionic emulsifier, Slovasol 2430 (Table II), directs the polymetization towards the homopolymer formation. The system containing $FeSO_4$–1,8-diamino-3,6-diazaoctane and Slovasol 2430 (Table III) as well as those consisting of $FeSO_4$–disodium ethylenediaminetetraacetic acid and Mersol H (Table II) exhibit a certain similarity by forming both types of polymers in comparable amounts. The presence of solvents has, in most cases, little effect on this behaviour. Frequently, the presence of solvents enhances, however, the efficiency of modification when compared with the systems without solvent. This is mainly due to the restriction of homopolymerization reaction. On the other hand, such an influence of components upon the polymerization is not typical for the case of water-soluble monomers, acrylic and methacrylic acids, acrylamide and methacrylamide (Tables I and III). They represent an exceptional group since their polymerization leads always to a predominant formation of bonded polymer, regardless the polymerization system used.

The system containing $FeSO_4$–disodium ethylenediaminetetraacetic acid activator with Mersol H is particularly notable (Table II). It serves a suitable example as to the influence of monomer structure on the degree of conversion and, particularly, the mutual ratio of both polymer types. While low-polar styrene and α-methylstyrene, resp., form almost exclusively the homopolymer, the medium polarity monomers, such as acrylic and methacrylic esters, give rise to both polymer types in comparable amounts. Finally, strongly polar, water-soluble monomers (acids and amides) form, under given conditions, predominantly polymer grafts. (Part of the runs shown in Table II was carried out only up to initial stages of reaction. So, after 20 min of reaction time it was found that the mutual ratio of homo- *vs* bonded polymer was identical to that after 6 hours. This allowed to compare these conversions at certain time.)

When interpreting these results, it is necessary to take into account the fact that geminal hydroperoxidic groups present on tertiary carbon atoms of polypropylene are associated *via* hydrogen bonding[12,13]. Such hydroperoxide (P—OOH, where P is propylene unit), will be decomposed by the ferrous chelate such as disodium ethylenediaminetetraacetic acid to give polymeric PO• radical:

$$\text{P—OOH} + \text{Fe}^{2+}\text{-chelate} \rightarrow \text{PO}^\bullet + \text{HO}^- + \text{Fe}^{3+}\text{-chelate}\,. \qquad (A)$$

The polymeric radical may either react with monomer (M)

$$\text{PO}^\bullet + \text{M} \rightarrow \text{modified PP} \qquad (B)$$

or it may induce the decomposition of geminal hydroperoxide by some of the following reactions[14]

$$\text{PO}^\bullet + \text{POOH} \rightarrow \text{POH} + \text{POO}^\bullet \begin{array}{l} \nearrow\ \text{POOP} + \text{O}_2 \\ \searrow\ \text{PO}^\bullet + \text{O}_2 \end{array} \qquad (C)$$

$$\text{PO}^\bullet + \text{POOH} \rightarrow \text{POOP} + \text{OH}^\bullet \qquad (D)$$

If the low molecular OH• radical initiates the polymerization (reaction (*E*)) then only homopolymer is formed.

$$OH^{\bullet} + M \rightarrow \text{homopolymer} \qquad (E)$$

Reactions (*A*), (*C*), and (*D*) will lead to a rapid decomposition of polypropylene hydroperoxide at the beginning of polymerization which is in accordance with the experimental data[15]. The observed high reactivity of the associated hydroperoxide[4], as well as its low thermal stability[16], may be attributed to its susceptibility to the induced decomposition.

It may be assumed that the presence of a strongly polar monomer solvating POOH at the site where reaction (*A*) is proceeding will enhance the formation of bonded polymer *via* reaction (*B*). On the other hand, when a monomer of low polarity is employed, its concentration at the reaction site will be unsufficient and reactions (*D*) and (*E*) will become significant thus enhancing the homopolymerization.

Other, apparently more stable polypropylene peroxides such as isolated hydroperoxides or dialkyl peroxides of P—OO—P′ type are decomposed practically only in the presence of alkalic chelate $FeSO_4$–1,8-diaminodiazaoctane[4] by the same mechanism as in (*A*). This leads exclusively to the formation of the bonded polymer according to reaction (*B*) as the processes (*D*) and (*E*) are considerably restricted. It is assumed that a relatively small quantity of homopolymer which is still formed is originated from the parallel reaction of the associated hydroperoxide with free $FeSO_4$ or 1,8-diamino-3,6-diazaoctane which are present in the system as a result of equilibrium with chelate[17].

The $FeSO_4$–1,8-diamino-3,6-diazaoctane chelate efficiently decomposes the associated hydroperoxides but from the viewpoint of modification this feature may be of significance only when strongly polar monomers are used. When styrene is employed, then this decomposition is inefficient even from the point of view of homopolymerization[4], probably because of the reaction of the activator or its components with low molecular radicals at the very moment of their formation on polypropylene surface[18]. Equally inefficient is the peroxide decomposition by the chelate in higher oxidation state:

$$POOH + Fe^{3+}\text{-chelate} \rightarrow PO_2^{\bullet} + H^+ + Fe^{2+}\text{-chelate}\,. \qquad (F)$$

Although this process regenerates the original chelate form, a relatively low reactive radical is formed. Reaction (*F*) is, however, necessary for the alkalic chelate which would otherwise undergo immediate hydrolysis[19].

Apart from the polarity of monomer, also its reactivity will be reflected on the results of polymerization (Table II). The systems forming one dominating polymer type $FeSO_4$–disodium ethylenediaminetetraacetic acid and Slovasol 2430 (Table II), and $FeSO_4$–1,8-diamino-3,6-diazaoctane with Mersol H (Table III), serve an example confirming a general relationship between the monomer reactivity and the rate of its polymerization, regardless the type of polymer formed, the activator, emulsifier and pH value of the emulsion.

TABLE IV

The influence of chelating agents (EDTA = disodium ethylenediaminetetraacetic acid, polyamine = 1,8-diamino-3,6-diazaoctane) and emulsifiers (ionic = Mersol H, non-ionic = Slovasol 2430) at the polymerization of alkylacrylates and methacrylates in the presence of ethyl acetate for 6 hours. Symbols: *e* average value of monomer polarity[9,10], *Q* general reactivity of monomer[9,10]

Ester	*e*	*Q*	Bonded polymer, % / Homopolymer, %			
			Mersol H		Slovasol 2430	
			EDTA	polyamine	EDTA	polyamine
			Acrylates			
Methyl	0·60	0·42	66·3	87·3	1·9	33·0
			24·7	11·5	78·9	39·1
Ethyl	0·22	0·52	46·0	84·7	2·0	26·8
			40·0	11·3	79·9	40·0
Propyl	0·72	0·66	28·7	79·2	2·4	20·3
			61·0	11·6	88·0	43·2
Butyl	1·06	0·50	21·8	77·4	2·4	17·4
			63·7	16·0	88·8	49·4
Pentyl	—[a]	—[a]	16·4	68·8	2·7	12·5
			58·7	19·7	84·0	57·8
			Methacrylates			
Methyl	0·40	0·74	55·9	69·5	3·7	15·5
			22·3	3·1	49·3	7·3
Ethyl	0·52	0·73	48·2	85·1	1·8	12·6
			35·7	6·1	62·0	12·8
Propyl	0·44	0·65	26·1	91·3	1·2	11·9
			55·8	8·7	80·7	17·2
Butyl	0·51	0·78	16·7	89·6	1·1	9·5
			68·0	9·2	91·4	27·6
Pentyl	0·43	0·68	13·1	61·6	1·0	8·4
			70·0	10·0	89·5	39·4

[a] The values of *e* and *Q* not available.

Other results presented in Table IV concerning the polymerization of acrylic and methacrylic esters indicate that even at similar values of *e* and *Q* for monomers, considerably different values of degree of conversion may be obtained; inversely, very close degree of conversion may be achieved even when the above mentioned characteristic constants are significantly differring. This signifies that also other factors, such as steric ones, are involved which are equally important and reflect structural properties of monomer influencing its ability to polymerize under given conditions.

The subsequent initiation efficiency of radicals formed in reactions (*A*), (*C*) and (*D*) will be strongly influenced by the character of emulsifier used. Slovasol 2430 creates more suitable conditions for the polymerization in aqueous emulsion than Mersol H as it contains polar poly(oxyethylene) chains and has a higher molecular weight. It is manifested by a more enhanced homopolymerization in the presence of this emulsifier when compared to the systems containing Mersol H, particularly when monomers with a limited water solubility are used. At the same time the use of Slovasol 2430 has a negative effect, unlike Mersol H, upon the polypropylene modification, certain water-soluble monomers being an exception (Table III). In the latter case, the polar groups of this emulsifier come into play by interacting with strongly polar monomer and polymer groups[20,21]. Mersol H with its short polar —SO_3Na group creates preferably favourite situation for the modification reaction on the polypropylene surface where it assists the contact of the reacting components[2]. From Table III it follows, however, that the use of strongly polar monomers represents in some cases serious limitations as to the use of this emulsifier type. The evaluation of the involvement of emulsion system in the process of formation of the above mentioned polymers requires to consider also the role of the water-insoluble phase. The latter may influence the concentration of components in the individual phase of the system and also the monomer and radical reactivities. This is reflected in the polymerization results which sensitively respond to each change of reaction conditions. The informative value is, moreover, enhanced by the simultaneous formation of two polymer types.

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REFERENCES

1. Citovický P., Mikulášová D., Chrástová V.: Chem. Zvesti *27*, 268 (1973).
2. Citovický P., Mikulášová D.: Chem. Zvesti *22*, 605 (1968).
3. Chrástová V., Mikulášová D., Citovický P.: *Collection of Works of the Faculty of Chemical Technology of the Slovak Technical University*, p. 189. Bratislava, 1975—1976.
4. Citovický P., Mikulášová D., Chrástová V., Řezníček J., Benč G.: Eur. Polym. J. *13*, 661 (1977).
5. Citovický P., Chrástová V., Mejzlík J., Majer J., Benč G.: This Journal *45*, 2319 (1980).
6. Citovický P., Mikulášová D., Chrástová V., Mejzlík J.: *Vth International IUPAC Conference on Modified Polymers*, Bratislava 1979. Preprints of Short Contributions, Vol. I, p. 89.

7. Citovický P., Mikulášová D., Chrástová V., Benč G.: Eur. Polym. J. *13*, 655 (1977).
8. Mikulášová D., Gheorghiu M.: Chem. Zvesti *18*, 614 (1964).
9. Young L. J.: J. Polym. Sci. *54*, 411 (1961).
10. Young L. J. in the book: *Polymer Handbook* (E. G. Immergut, J. Brandrup, Eds), p. II-387. Interscience, New York—London—Sydney 1975.
11. Janda J.: *Vinylové monoméry*, pp. 46, 76, 258 and 284. Slovenské vydavatelstvo technickej literatury, Bratislava 1958.
12. Chien J. C. W., Vandenberg E. J., Jabloner H. J. Polym. Sci. A 1, *6*, 381 (1968).
13. Chien J. C. W., Boss C. R., Jabloner H., Vandenberg E. J.: J. Polym. Sci., Polymer Lett. Ed. *10*, 915 (1972).
14. Hiatt R., in the book: *Organic Peroxides* (D. Swern, Ed.), Vol. 21, p. 86. Interscience, New York, London, Sydney, Toronto 1971.
15. Mikulášová D., Chrástová V., Citovický P.: Eur. Polym. J. *10*, 551 (1974).
16. Citovický P., Mikulášová D., Chrástová B.: Eur. Polym. J. *12*, 627 (1976).
17. Šimek I., Citovický P., Lipták P. This Journal *43*, 2565 (1878).
18. Citovický P., Šimek I., Mikulášová D., Chrástová V., Řezníček J.: Chem. Zvesti *28*, 802 (1974).
19. Mikulášová D., Citovický P.: Chem. Zvesti *20*, 37 (1966).
20. Orther J.: Melliand Textilber. *31*, 263 (1950).
21. Wurzschmidt B.: Fresenius' Z. Anal. Chem. *130*, 105 (1950).

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