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Vinyl Polymerization. CLXXIII. Effects of Water and Some Reducing Agents on the Polymerization of Vinyl Monomers Initiated by Nickel Peroxide

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Summary

The polymerization of vinyl monomers such as styrene, methyl methacrylate, acrylonitrile, vinyl acetate, and vinyl chloride was carried out in the presence of water with nickel peroxide as a solid radical initiator. It was found that the rates of polymerizations of the monomers markedly increased with the presence of water, except in the case of styrene, and the molecular weights of the polymers obtained in water were higher than those obtained in toluene. The accelerating effect of water was closely related to the solubility of the monomer used in water. The stereoregularities of the polymers resulting from methyl methacrylate, however, were observed to be rather random. The effects of some organic and inorganic reducing agents on the rate of polymerization of methyl methacrylate or styrene initiated by nickel peroxide, and on the molecular weight and the stereoregularity of the resulting polymers were also investigated.

Nickel peroxide (Ni-PO) was prepared by oxidation of nickel sulfate with sodium hypochlorite in water, followed by drying in a stream of nitrogen at room temperature. Ni-PO obtained in this way was a fine black powder and insoluble in water and most organic solvents. In 1964 we found that Ni-PO could act as an effective solid radical initiator for vinyl monomers and produce an isotactic polymer from styrene (1). This result was explained by the

basis of the stereospecific adsorption of monomers on the surface of Ni-PO. If Ni-PO has both sites for producing a radical and for adsorbing the monomer stereospecifically, it may be expected that there are some interesting features are not observed in polymerization by ordinary soluble radical initiators. Some of them have already been reported (2-6).

However, the catalytic activity of Ni-PO as a radical initiator is lower than that of an ordinary one. It is necessary to enhance the catalytic activity of Ni-PO, especially at lower temperatures, because its adsorption with the monomer is considered to become important at lower temperatures. For this purpose we have made some attempts to improve the catalytic activity of Ni-PO and found that the binary catalyst systems, such as Ni-PO-Ziegler catalyst or Ni-PO-organometallic compounds, are effective initiators even at temperatures below 0°C (5). In this case, if the radicals available to chain initiation are produced by a redox mechanism, some organic and inorganic reducing agents are expected to accelerate the radical decomposition of Ni-PO.

Recently we have also found that the rate of polymerization markedly increases when the polymerizations of some vinyl monomers initiated by Ni-PO are performed in water. The present paper describes the effects of water and some reducing agents on the polymerization of methyl methacrylate (MMA), styrene (St), acrylonitrile (AN), vinyl acetate (VAC) and vinyl chloride (VC) initiated by Ni-PO and on the stereoregularity of the polymers obtained from MMA.

EXPERIMENTAL

Materials

Nickel peroxide (Ni-PO) was prepared according to the method described in the previous papers (2). Monomers and solvents used in this study were purified by the usual methods. Water was used after purification by passing through ion-exchange resins, followed by distillation. All other reagents, which were analytical grade, were used without further purification.

Polymerization Procedure

Polymerizations were carried out in a sealed glass tube under

shaking in a thermostat maintained at a given temperature. After polymerization for a given time, the polymerized mixtures, except for VAC, were poured into a large amount of methanol containing hydrochloric acid to precipitate the polymer and to dissolve the residual Ni-PO. In the case of VAC, a large amount of methanol was added to the polymerized mixture and then filtered to remove the Ni-PO and inorganic materials.

The polymer obtained in this way was purified further several times by a reprecipitation method.

Determinations of Intrinsic Viscosity and Stereoregularity

Intrinsic viscosities ($[\eta]$) of the polymers were determined in suitable solvents indicated below, and the degree of polymerization was calculated from the following equations:

$$\text{poly(MMA) (7): } [\eta] = 2.5 \times 10^{-3} \bar{P}_n^{0.8} \text{ (in chloroform } 20^\circ\text{C)}$$

$$\text{poly(St) (8): } [\eta] = 1.7 \times 10^{-4} \bar{M}_n^{0.69} \text{ (in toluene } 25^\circ\text{C)}$$

$$\text{poly(AN) (9): } [\eta] = 1.66 \times 10^{-4} \bar{M}_n^{0.81} \text{ (in dimethylformamide } 25^\circ\text{C)}$$

$$\text{poly(VAC) (10): } [\eta] = 5.02 \times 10^{-4} \bar{M}_n^{0.62} \text{ (in acetone } 25^\circ\text{C)}$$

$$\text{poly(VC) (11): } \bar{P}_n = 500(\text{antilog}[\eta]/0.168 - 1) \text{ (in nitrobenzene } 30^\circ\text{C)}$$

Syndiotacticity of the resulting poly (MMA) was determined by its infrared spectrum according to the method of Watanabe (12).

RESULTS AND DISCUSSION

Effect of Water on the Polymerization Initiated by Ni-PO

In the previous papers (1-6), all the experiments in which Ni-PO was used as an initiator were performed in organic solvent or in bulk. In the present work, the polymerizations of vinyl monomers were carried out in water, toluene, and their mixtures, in which the concentration of monomer was kept constant. The results are shown in Table 1.

As can be seen from this table, the yield of the polymers obtained in water, except for St, were higher than those in toluene. Such a remarkable acceleration in aqueous polymerization, as compared with the polymerization in toluene, was observed in the polymerizations of MMA, AN, VAC, and VC. This effect was considered to

TABLE I
Effect of Water on the Polymerization of Vinyl Monomers Initiated by Ni-PO

Run	Monomer	ml	Ni-PO, ^a g	System		Polymerization		Polymer		
				Toluene, ml	Water, ml	Temp., °C	Time, hr	Yield, %	\bar{P}_n	Syndiotac- tivity, %
1-1	MMA	5	0.5	5	0	30	4	15.4	1700	53
2		5	0.5	4	1	30	4	5.9	1900	47
3		5	0.5	3	2	30	4	8.8	4500	48
4		5	0.5	2	3	30	4	17.0	5300	48
5		5	0.5	1	4	30	4	15.1	5700	49
6		5	0.5	0	5	30	4	36.7	8100	47
2-1	AN	5	0.5	5	0	60	3	3.9	560	—
2		5	0.5	4	1	60	3	13.7	790	—
3		5	0.5	3	2	60	3	19.5	2840	—
4		5	0.5	2	3	60	3	31.2	3350	—
5		5	0.5	1	4	60	3	47.0	3600	—
6		5	0.5	0	5	60	3	~100	4320	—
3-1	VAC	5	0.5	5	0	60	3	3.4	250	—
2		5	0.5	4	1	60	3	19.9	380	—
3		5	0.5	3	2	60	3	25.0	420	—
4		5	0.5	2	3	60	3	40.0	470	—
5		5	0.5	1	4	60	3	47.0	700	—
6		5	0.5	0	5	60	3	90.9	2330	—
4-1	VC	5	0.5	5	0	60	16	32.5	450	—
2		5	0.5	4	1	60	16	11.8	1100	—
3		5	0.5	3	2	60	16	9.8	2000	—
4		5	0.5	2	3	60	16	12.0	2300	—
5		5	0.5	1	4	60	16	34.4	3300	—
6		5	0.5	0	5	60	16	~100	3000	—
5-1	St	5	0.5	5	0	60	24	1.4	2200	—
2		5	0.5	4	1	60	24	1.0	3500	—
3		5	0.5	3	2	60	24	1.9	3800	—
4		5	0.5	2	3	60	24	1.4	4800	—
5		5	0.5	1	4	60	24	0.9	9700	—
6		5	0.5	0	5	60	24	1.6	10000	—

^a Active oxygen content of Ni-PO was 0.0036 g-atom/g.

be closely related to the solubility of the monomers used in water, as indicated in Table 2. No acceleration for aqueous polymerization of St can be explained by its low solubility in water.

In the oxidation of alcohols in water by Ni-PO, it was reported that their solubilities in water were related to their oxidation rates (15). This observation was in good agreement with that obtained in the present study for the vinyl polymerization by Ni-PO.

Figure 1 shows the relationship between the rate of polymerization and the ratio of water to toluene as polymerization medium. From this figure it was found that the rates of polymerization of AN and VAC increased linearly with an increase of the concentration

TABLE 2
Effects of Solubilities of Monomers in Water on
Yields for the Polymerization

Monomer	Solubility in water, %	Y_H/Y_T^c
AN	7.35 (20°C) ^a	25.6
VAC	2.5 (28°C) ^a	26.7
MMA	1.5 (30°C) ^a	2.4
VC	~0.6 (50°C) ^b	3.1
St	0.0125 (20°C) ^a	1.0

^a From data of Blout and Mark (13).

^b From data of Peggion et al. (14).

^c Y_H and Y_T , yield of polymer obtained in water and toluene, respectively.

of water, but those of MMA and VC decreased initially at the lower concentration of water and then increased. The explanation for giving a minimum in the latter cases was not possible at the present time, because these polymerizing system are too complicated.

The molecular weights of all the resulting polymers increased as a function of the concentration of the added water, as indicated in Fig. 2. This result might suggest that the rate of termination de-

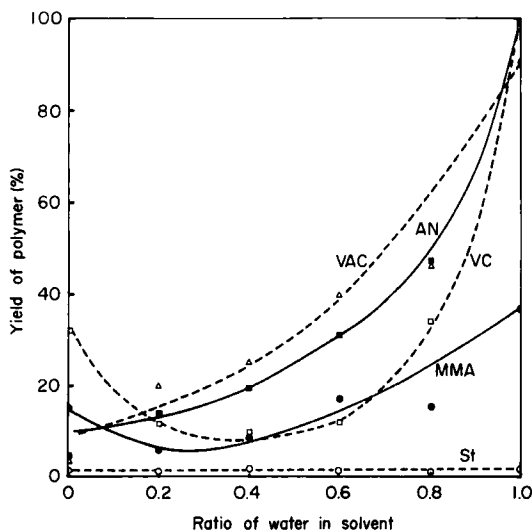


FIG. 1. Effect of water on the rate of polymerization of VAC (Δ), AN (\blacksquare), VC (\square), MMA (\bullet), and St (\circ).

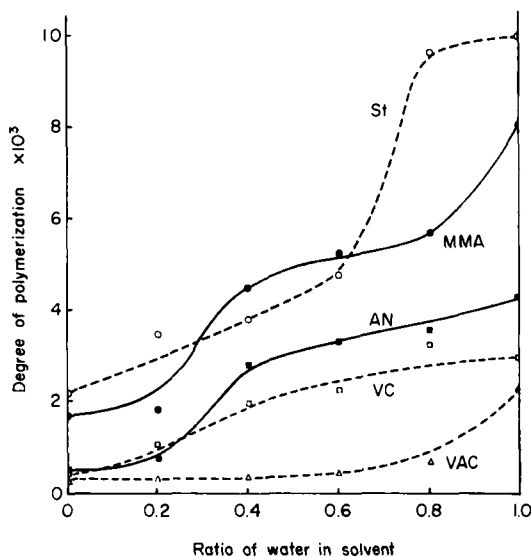


FIG. 2. Effect of water on the degree of polymerization (\bar{P}) of VAC (Δ), AN (\blacksquare), VC (\square), MMA (\bullet), and St (\circ).

increased in the presence of water, the same as in ordinary suspension polymerization. This might be one of the possible reasons for observing such an acceleration in water.

Recently it was found that the active oxygen (O^*) in Ni-PO available for initiating the polymerization decreased as the content of water in Ni-PO decreased (2).

To clarify this point further, the correlation between the polymerization activity and the water content of Ni-PO was investigated. MMA was used as monomer and Ni-PO was used after drying in atmospheric pressure at room temperature for a different time. The results are shown in Table 3.

From Table 3, a similar correlation between the polymerization activity and the water content in Ni-PO was observed (see Table 1). However, when the Ni-PO was dried under reduced pressure (2 mm Hg) the rate was found to decrease as a function of the drying time (Table 4). Accordingly, it was clear that the presence of a suitable amount of water might also be an essential factor for enhancing the polymerization activity of Ni-PO.

From Table 4, when Ni-PO was dried under reduced pressure, it was understood that both water and active oxygen were eliminated

TABLE 3

Correlation between Polymerization Activity of Ni-PO and Its Water Content in the Polymerization of MMA

Drying time, hr	Water content in Ni-PO, ^a %	Apparent O ^o content, mg-atom/g Ni-PO	O ^o content per Ni atom, mg-atom/g Ni	Polymer yield, ^b %
0	67.6	2.06	8.72	10.0
6	66.9	2.11	8.69	0.6
18	62.8	2.43	8.92	3.3
66	37.3	3.37	7.57	8.0
72	32.0	3.40	6.62	7.0
115	23.8	3.54	6.33	11.1
120	23.9	3.54	6.33	11.1

^a Determined from the weight.^b Polymerized the mixture of MMA (5 ml), benzene (5 ml), and Ni-PO (0.38 g as completely dried Ni-PO) at 30°C for 4 hr.

from the Ni-PO. However, in all cases it was obvious that the polymerizations in water proceeded much faster than those in bulk and in benzene.

As can be seen from Fig. 1, it must be noted that the most remarkable acceleration in rate of polymerization by water is ob-

TABLE 4

Comparison between Polymerization Activity of Ni-PO and Its Water Content in the Polymerization of MMA

Drying time, hr	Water content in Ni-PO, ^a %	Apparent O ^o content, mg-atom/g Ni-PO	Polymer yield, % ^b in		
			Bulk	Benzene	Water
0	23.9	3.54	26.8	9.8	44.9
0.5	8.1	0.93	8.2	7.5	24.5
1	8.0	0.66	4.0	7.5	22.1
2	8.0	0.46	3.1	1.7	20.2
4	7.4	0.51	2.8	1.2	21.8
8	7.6	0.45	2.8	0.5	19.9
20	7.6	0.35	3.8	0.5	22.9

^a Dried under a reduced pressure (2 mm Hg) at room temperature.^b Polymerized at 30°C for 4 hr. 0.38 g Ni-PO was used as completely dried Ni-PO.

TABLE 5
 Polymerizations of MMA and AN in Some Solvents by Ni-PO
 ([MMA] = 4.68, [AN] = 8.01 moles/liter)

Ni-PO ^a	Polymer yield, % ^b					
	MMA in			AN in		
	Benzene	Water	Heptane	Benzene	Water	Heptane
A	9.8	44.9	38.6	5.2	~100	16.2
B	1.7	20.2	—	1.1	47.3	—
C	0.5	19.9	0.1	1.6	31.0	1.7

^a Samples A, B, and C correspond to those dried for 0, 2, and 8 hr, respectively (see Table 4).

^b Polymerized at 30°C for 4 hr in the case of MMA, and at 60°C for 3 hr in the case of AN.

served in the cases of AN and VC, whose produced polymers are insoluble in both water and toluene as solvents. To check whether the heterogeneity of the polymerizing system might be important in this case, the polymerization of MMA and AN in some solvents and a nonsolvent (*n*-heptane) was attempted. The results are shown in Table 5.

From the results of Table 5, it was understandable that these effects were not only due to the heterogeneity of the polymerization systems.

It was found from Table 1 that the syndiotacticities of poly(MMA) obtained were not widely changed by the concentration of water in the polymerization system of MMA by Ni-PO, but those decreased somewhat, as compared with ordinary radical polymers obtained in bulk at the same temperature. More detailed investigations have been reported in the previous paper (6).

Effects of Organic and Inorganic Compounds

To enhance the initiator activity of Ni-PO, the rates of decomposition of Ni-PO in organic solvents and of polymerization of St with these systems were determined. The results are shown in Table 6.

As can be seen from this table, the rate of decomposition of Ni-PO was markedly accelerated in the presence of polar solvents. The order of increase in the rate of decomposition with the kind of sol-

vent was in fairly good agreement with the reported order in the decomposition of benzoyl peroxide (16). However, a reverse correlation was approximately observed between the decomposition rate and the polymerization rate, suggesting that these binary systems initiate dead-end polymerization (17). From Table 6 it was also noted that no isotactic polymer (MEK-insoluble fraction) was produced in polar solvents other than benzene.

Similar results were obtained in the binary systems of Ni-PO and ordinary inorganic reducing agents, such as sodium thiosulfate, bisulfite, and sulfite, for the polymerization of St.

On the other hand, it was expected that the change in surface structure of Ni-PO would lead to a change in stereoregularity of the polymer obtained, because the stereospecific adsorption of the polymerizing monomers on the surface of a solid Ni-PO was considered to be an important factor for the production of stereoregular polymer by Ni-PO (2). In the hydrogenation by Raney nickel, it was reported that the addition of some inorganic salts increased the

TABLE 6
Effects of Organic Solvents on the Rate of Decomposition
of Ni-PO and of Polymerization of St

Solvents	Decomposition, % ^a		Polymeri- zation, ^b %	MEK-insoluble fraction, ^c %
	30 min	60 min		
Benzene	(0.94) ^d	(1.86) ^d	17.6	0.77
Pyridine	10	12	21.8	0
Carbon tetrachloride	10	16	5.0	0
Chloroform	28	45	35.4	0
Dimethylformamide	36	46	9.3	0
Dioxane	—	—	4.9	0
Ethyl acetate	55	63	—	—
Diglyme	60	74	6.4	0
Triethylamine	98	100	16.0	0

^a Determined by the method described in the previous paper (2). The mixture of 0.2 g of Ni-PO and 5 ml of solvent was decomposed at 60°C in a sealed tube.

^b Polymerized the mixture of 1 g of Ni-PO, 1 ml of solvent, and 10 ml of St in sealed tube at 60°C for 26 hr.

^c Extracted with methyl ethyl ketone (MEK).

^d Determined in St.

TABLE 7

Aqueous Polymerization of MMA Initiated by Ni-PO in the Presence of Inorganic Salts ($[MMA] = 4.68$, $[H_2O] = 27.8$ moles/liter, $30^\circ C$, 4 hr)

Run	Inorganic salts	moles/ liter	Polymer		
			Yield, %	$[\eta]$ dl/g	Syndio- tacticity, %
6-1 ^a	CoSO ₄ ·7H ₂ O	0	36.7	3.3	46
2		0.05	41.5	2.6	47
3		0.10	52.5	3.2	47
4		0.21	62.1	3.3	54
5		0.43	27.0	3.3	45
6		0.85	24.5	3.3	45
7		1.70	18.6	3.3	46
7-1 ^a	FeSO ₄ ·7H ₂ O	0.05	41.0	4.4	44
2		0.10	54.7	4.0	42
3		0.21	20.7	3.7	43
4		0.43	7.7	4.1	48
5		0.85	11.3	3.9	49
6		1.70	8.0	3.8	44
8-1 ^a		CdSO ₄ · $\frac{3}{2}$ H ₂ O	0.05	32.0	3.2
2	0.10		33.1	3.3	44
3	0.21		31.1	3.1	42
4	0.43		28.5	3.1	45
5	0.85		35.1	3.5	51
6	1.70		29.1	3.5	41
9-1 ^b	AgNO ₃		0.05	32.0	4.1
2		0.10	32.9	3.9	48
3		0.21	37.9	4.0	41
4		0.43	45.2	4.0	47
5		0.85	55.3	3.8	44
6		1.70	29.3	4.0	44
10-1 ^c		NiSO ₄ ·7H ₂ O	0.05	20.1	3.5
2	0.10		23.4	3.6	48
3	0.20		27.5	3.6	43
4	0.40		12.8	3.3	48
5	0.80		7.8	3.1	50
6	1.60		4.6	3.1	49
11-1 ^c	CuSO ₄ ·5H ₂ O		0.05	22.0	3.6
2		0.10	36.7	3.6	46
3		0.19	33.5	3.6	49
4		0.38	15.2	3.3	47
5		0.75	37.7	3.3	43
6		1.50	32.4	3.4	47

^a $[Ni-PO] = 0.17$ g-atom/liter.

^b $[Ni-PO] = 0.17$ g-atom/liter. Reaction time was 2 hr.

^c $[Ni-PO] = 0.16$ g-atom/liter.

selectivity for hydrogenation because of the change in the surface structure of the catalyst (18,19).

Table 7 shows the results of polymerization of MMA in water in the presence of some inorganic salts. From this table, ferrous sulfate, cobaltous sulfate, and silver nitrate were found to accelerate the rate of polymerization as the result of a redox decomposition of Ni-PO. However, molecular weight and the stereoregularity of the polymers were not affected by the addition of these salts.

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REFERENCES

1. M. Imoto, T. Otsu, T. Nakata, and Y. Kinoshita, *J. Polymer Sci.*, **B2**, 227 (1964).
2. T. Nakata, T. Otsu, and M. Imoto, *J. Polymer Sci.*, **A3**, 3383 (1965).
3. T. Nakata, Y. Kinoshita, T. Otsu, and M. Imoto, *Kogyo Kagaku Zasshi*, **68**, 864 (1965).
4. T. Nakata, T. Otsu, and M. Imoto, *J. Macromol. Chem.*, **1**, 553 (1966).
5. T. Nakata, T. Otsu, and M. Imoto, *J. Macromol. Chem.*, **1**, 563 (1966).
6. T. Nakata, T. Otsu, M. Yamaguchi, and M. Imoto, *J. Macromol. Sci.*, **A1**, 1447 (1967).
7. S. Baysal and A. V. Tobolsky, *J. Polymer Sci.*, **9**, 171 (1952).
8. P. Outer, C. I. Carr, and B. H. Zimm, *J. Chem. Phys.*, **18**, 830 (1950).
9. J. Bischops, *J. Polymer Sci.*, **17**, 81 (1955).
10. A. Nakajima, *Kobunshi Kagaku*, **6**, 451 (1949).
11. I. Sakurada, J. Matsuda, S. Matsumoto, and T. Chiba, *Kogyo Kagaku Zasshi*, **47**, 133 (1944).
12. H. Watanabe, *Kogyo Kagaku Zasshi*, **64**, 1851 (1961).
13. E. R. Blout and H. Mark, *Monomers*, Wiley (Interscience), New York, 1951.
14. E. Peggion, F. Festa, and G. Talamini, *Makromol. Chem.*, **71**, 173 (1964).
15. K. Nakagawa, R. Konaka, and T. Nakata, *J. Org. Chem.*, **27**, 1597 (1962).
16. K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.*, **68**, 1686 (1946).
17. K. F. O'Driscoll and J. F. Schmidt, *J. Polymer Sci.*, **45**, 189 (1960).
18. K. Taya, H. Masaki, and T. Yamanaka, *Sci. Papers Inst. Phys. Chem. Res. (Japan)*, **55**, 105 (1961).
19. B. B. Elsner and P. F. M. Paul, *J. Chem. Soc.*, **1953**, 3156.

Zusammenfassung

Die Polymerisation von Vinylmonomeren, wie z.B. Styrol, Methylmethacrylsäurester, Acrylnitril, Vinylacetat und Vinylchlorid wurde in Gegenwart von Wasser mit Nickelperoxid als festem Radikalstarter durchgeführt.

Die Polymerisationsgeschwindigkeiten der Monomeren erhöhte sich merklich in Gegenwart von Wasser—ausgenommen bei Styrol—und die Molekulargewichte der in Wasser erhaltenen Polymeren waren höher als die von in Toluol erhaltenen. Dieser beschleunigende Effekt des Wassers steht in enger Beziehung zu der Löslichkeit des verwendeten Monomeren in Wasser. Die Stereoregularität der aus Methylmethacrylat erhaltenen Polymeren wurde jedoch zunehmend statistisch. Ebenfalls untersucht wurde der Einfluss einiger organischer und anorganischer Reduktionsmittel auf die Polymerisationsgeschwindigkeit von Methylmethacrylat oder Styrol (mit Nickelperoxid gestartet) und die Molekulargewichte als auch die Stereoregularität der erhaltenen Polymeren.

Résumé

Polymérisation des monomères vinyliques tels que le styrène, le méthacrylate de méthyl, l'acrylonitrile, l'acétate, de vinyl, et le chlorure de vinyl en présence d'eau à l'aide du peroxyde de nickel comme initiateur radicalaire solide. On a trouvé que les vitesses de polymérisations des monomères sont considérablement augmentées en présence d'eau, sauf dans le cas de styrène, et aussi que les masses moléculaires des polymères obtenus dans l'eau sont plus élevées que des polymères préparés dans le toluène. L'effet accélérateur de l'eau est étroitement lié à la solubilité du monomère utilisé dans ce solvant. On a observé, que les stéréorégularités des polymères obtenus à partir du méthacrylate de méthyl deviennent plutôt désordonnées. On a aussi examiné les effets de quelques agents réducteurs organiques et inorganiques sur la vitesse de polymérisation du méthacrylate de méthyl ou du styrène, initiée par le peroxyde de nickel, sur la masse moléculaire et sur la stéréorégularité des polymères obtenus.

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