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Summary

When nickel peroxide was used as an initiator of the polymerization of methyl methacrylate, it was found that the radical polymerization proceeded easier than styrene under similar conditions, and that the polymers obtained at low temperatures showed somewhat increased syndiotactic sequence as compared with ordinary radical polymers. From the NMR determinations of the polymers resulted by nickel peroxide at various temperatures, the Bovey-Tiers relationship, that is, that the probabilities of formation of isotactic, syndiotactic, and heterotactic triads of monomer unit among the polymer chain are controlled by a single parameter of the probability of isotactic addition of monomer in the propagation step was confirmed in this case. Similarly, the ratio k_i/k_s in rate constants for isotactic and syndiotactic additions in the polymerization by nickel peroxide in bulk was expressed by the following equation:

$$k_i/k_s = 1.31 \exp(-1.17 \text{ kcal}/RT)$$

In this equation, the difference in activation energy and entropy were somewhat larger than those reported for ordinary radical polymerization. These results might be understandable if the monomers adsorbed on the solid nickel peroxide were favored to enter to the syndiotactic propagation.

In the polymerization of styrene initiated by nickel peroxide (Ni-PO) as a solid radical initiator, it was found to be obtained as an isotactic polymer (*1*). Such stereoregulating effects of the Ni-PO were also observed in the polymerizations of butadiene (*2*), isoprene (*2*), vinyl acetate (*3*), and vinyl chloride (*4*). In the previous paper (*5*) it was reported from the copolymerization experiment that Ni-PO could induce the radical polymerization of methyl methacrylate. The present paper describes the effect of Ni-PO on the stereoregularity of the polymerization of methyl methacrylate at various temperatures.

EXPERIMENTAL

The preparation of the Ni-PO and the determination of its active oxygen content (O^* g-atom/g of Ni-PO), which was used as the initiator concentration available for polymerization, were carried out according to the method described in the previous paper (*1*).

Methyl methacrylate (MMA) was fractionally distilled under reduced pressure before use, and the other reagents were purified by distillation.

Polymerizations were carried out in sealed glass tubes under shaking in a thermostat maintained at a given temperature. The resulting polymer was isolated by the addition of a large amount of methanol, followed by the decomposition of the Ni-PO with a large amount of methanol containing 3 vol. % of concentrated hydrochloric acid. The resulting polymer was then purified by reprecipitating from acetone with petroleum ether.

The stereoregularity of the resulting poly(methyl methacrylate) (PMMA) was estimated from the NMR spectra, which were recorded in deuterated chloroform solution by using a Varian A-60, according to the method of Bovey and Tiers (*6*). IR spectra of the polymers were also used for determining their stereoregularities, according to the treatment of Goode et al. (*7*).

Number-average degree of polymerization ($\bar{P}_n$) was calculated from the Baysal-Tobolsky equation (*8*), by using the intrinsic viscosity determined in chloroform solution at 30°C. The glass transition temperatures (T_g) and melting points (T_m) of the resulting PMMA were determined by the dilatometric method and the hotplate method, respectively.

RESULTS AND DISCUSSION

The results of the polymerization of MMA initiated by Ni-PO at various temperatures and of the structural parameters of the result-

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TABLE 1

Results of Polymerization of MMA with Ni-PO ([MMA] = 1.82 moles/liter in toluene)

Initiator[a]	Polymerization Temp., °C	Polymerization Time, hr	Conversion, %	$\bar{P}_n$	Infrared[b] J value	T_m, °C	T_g, °C	Polymer structure[c]
Ni-PO	80	6	86.5	320	104	—	—	*s*
Ni-PO	60	8	78.3	430	104	178–189	115	*s*
Ni-PO	20	18	53.4	—	108	190	115	*s*
Ni-PO	10	24	25.0	—	112	190	115	*s*
Ni-PO	0	36	17.8	—	110	190	115	*s*
BPO	100	8	91.6	140	98.7	—	104	*h*
PhMgBr	3	4	73.5	2060	27.7	160	45	*i*
PhMgBr	−78	4	12.1	650	48.5	170	79–95	*is*

[a] Initiator concentrations are as follows: [Ni-PO] = 0.18 O^* g-atom/liter, [BPO] = 0.02 mole/liter, and [PhMgBr] = 0.02 mole/liter in toluene.

[b] Determined from IR spectra of PMMA films according to the method of Goode et al. (7).

[c] Estimated from the J value: *i*, isotactic; *s*, syndiotactic; *h*, heterotactic; *is*, stereoblock.

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ing polymers are shown in Table 1, in which the results obtained by benzoyl peroxide (BPO: soluble radical initiator) and phenyl magnesium bromide (PhMgBr: anionic catalyst) are also indicated.

When Ni-PO was used as an initiator of the polymerization of MMA, it was found that the radical polymerization proceeded easier than styrene (*1*) under similar conditions.

Infrared spectra of the polymers obtained by using the different initiators are shown in Fig. 1, from which their J values were determined by the method reported by Goode et al. (7) as indicated in Table 1. As can be seen this table, the polymers obtained by Ni-PO gave higher J values as compared with those by other initiators, indicating that these polymers are rich in syndiotactic sequence. This result corresponds to the observed differences in the glass transition and melting temperatures of the polymers (see Table 1) and in NMR spectra, as shown in Fig. 2.

To further clarify the stereoregulating effect of Ni-PO, the polymerizations were carried out in bulk and in water at various temperatures and the stereoregularities of the polymers were determined

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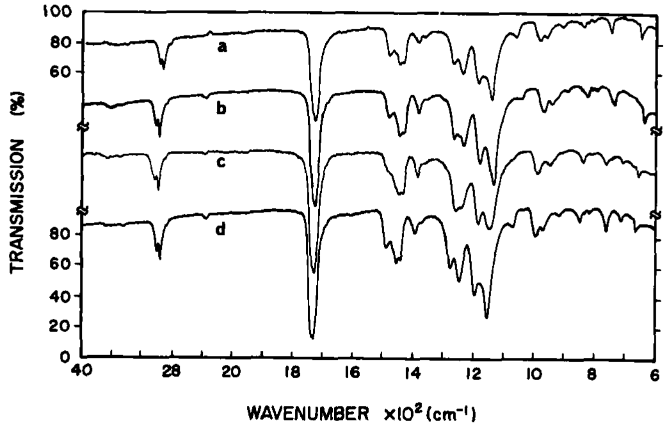

FIG. 1. Infrared spectra PMMA obtained by using different initiators: (a) syndiotactic PMMA obtained by Ni-PO at 0°C; (b) stereoblock PMMA obtained by PhMgBr at −78°C; (c) isotactic PMMA obtained by PhMgBr at 3°C; (d) heterotactic PMMA obtained by BPO at 100°C.

by their NMR spectra according to the treatment by Bovey and Tiers (*6*). The results are shown in Table 2. The effect of water on the vinyl polymerization will be described in the next paper (*9*).

Comparing the result of Table 2 with the reported result under the same temperature (*6,10*), the PMMA obtained by Ni-PO in bulk were found to be rich in syndiotactic sequence, but those obtained

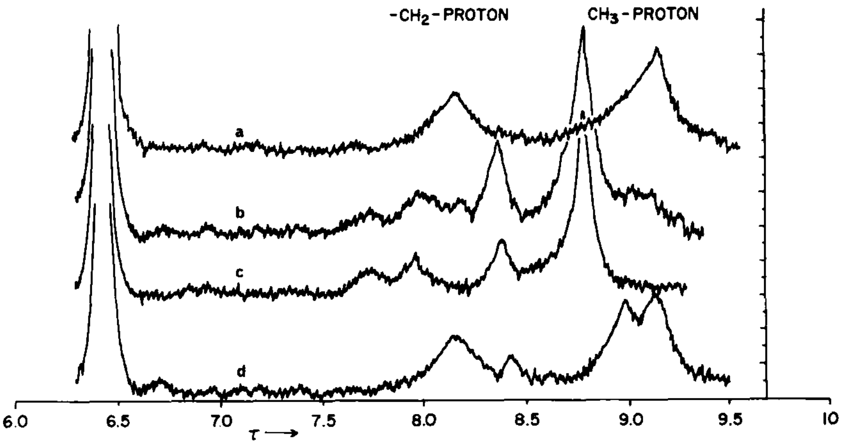

FIG. 2. NMR spectra of PMMA (in 3% deuterated chloroform solution, 60 Mc, at 25°C); (a), (b), (c), and (d) are the same as those indicated in Fig. 1.

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TABLE 2

Effect of Ni-PO on the Stereoregularities in the Polymerization of MMA ([Ni-PO] = 0.43 O* g-atom/liter)

	Polymerization					Tacticity, %[a]			
Run	Temp., °C	Time, hr	Conversion, %	Rate of polymerization, %/hr	$\bar{P}_n$	P_s	P_h	P_i	σ^b
			In bulk ([MMA] = 9.36 mole/liter)						
1	80	0.75	19.4	25.8	380	71.6	22.0	6.4	0.152
2	60	1.25	22.4	17.9	900	75.2	19.3	5.5	0.132
3	40	2.00	15.0	7.5	1600	77.0	19.2	3.8	0.116
4	20	4.92	11.1	2.3	2800	79.6	16.0	4.4	0.105
5	10	10.0	16.8	1.7	4000	82.1	15.6	2.3	0.094
6	0	18.3	13.5	0.74	4500	82.6	14.2	3.2	0.091
7	−78	31.8	0.41	0.013	—	86.7	9.8	3.5	0.068
			In water ([MMA] = 4.68 mole/liter)						
8	80	0.75	17.4	23.2	6100	56.2	35.7	8.0	0.248
9	60	1.25	19.4	11.4	6400	58.8	34.0	7.2	0.231
10	40	2.00	15.9	8.0	8600	60.6	33.2	6.2	0.218
11	20	3.14	14.4	4.58	9000	68.1	27.5	4.4	0.170
12	10	6.26	18.9	3.02	12000	69.8	26.5	3.7	0.162
13	0	6.26	14.2	2.26	14000	70.5	24.8	4.7	0.157

[a] Determined from NMR spectra.

[b] Probability of isotactic addition of monomer in the propagation step.

in water did not give such marked differences. From Table 2 it was also observed that the syndiotactic sequence of the polymers increased with decreasing polymerization temperatures, the same as ordinary radical polymerization. However, this result was in marked contrast to that for styrene, which produced an isotactic polymer (*1*).

According to the treatment of Bovey and Tiers (*6*), if the stereochemical structure of the polymers is controlled by a single parameter of the probability of isotactic addition of monomer (σ) in the propagation step, the ratio in rate constants for isotactic and syndiotactic additions can be given by

$$\sigma/1 - \sigma = k_i/k_s \qquad (1)$$

where k_i and k_s are the rate constants for isotactic and syndiotactic additions, respectively. And the probabilities of formation of isotactic, syndiotactic, and heterotactic triads of monomer unit (P_i, P_s,

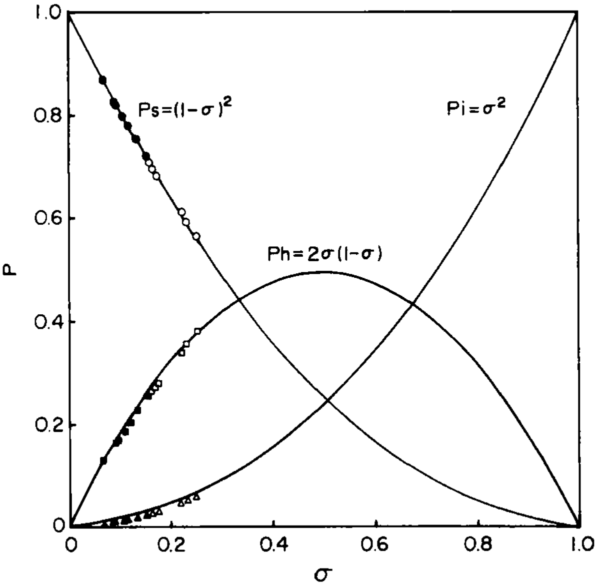

FIG. 3. Plot of the Bovey-Tiers relationship, Eqs. (2) to (4).

and P_h) can be expressed by

$$P_i = \sigma^2 \tag{2}$$

$$P_s = (1-\sigma)^2 \tag{3}$$

$$P_h = 2\sigma(1-\sigma) \tag{4}$$

To check whether the Bovey-Tiers relationships, Eqs. (2) to (4), are applicable in the polymerization by solid Ni-PO, the probabilities of formation of the respective triads (P_i, P_s, and P_h) shown in Table 2 were plotted as a function of the σ value. The results are shown in Fig. 3, from which the Bovey-Tiers relationship was confirmed to be established in the present system.

Then the temperature dependence of the rate constant ratio (k_i/k_s), which was determined by using the σ values in Eq. (1), was tested. The results are shown in Fig. 4, from which the following relationships were drawn:

In bulk:

$$k_i/k_s = 1.31\ \exp(-1.17\ \text{kcal}/RT) \tag{5}$$

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In water:

$$k_i/k_s = 0.34 \exp(-1.51 \text{ kcal}/RT) \tag{6}$$

As can be seen from Eqs. (5) and (6), the difference in activation energy, $(E_i - E_s)$, for the polymerization by Ni-PO was somewhat larger than the reported values [0.775 (*6*), 0.960 (*11*), and 1.040 kcal/mole (*10*)] for ordinary radical polymerization with azobisisobutyronitrile as an initiator. And also the difference in activation entropy might be important, especially in considering the observed discrepancy between bulk and water polymerizations. These results might be understandable if the monomers adsorbed on the solid Ni-PO were favored to enter the syndiotactic propagation. In this case it might also be useful to consider the syndiotactic adsorption of the reacting monomer.

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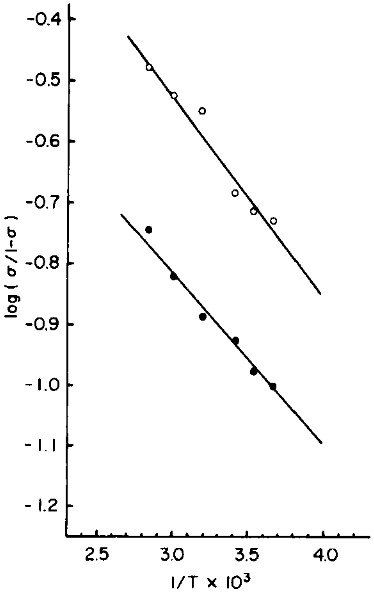

FIG. 4. Relationship between log ($\sigma/1 - \sigma$) and $1/T$ on the polymerization of MMA in bulk (●) and in water (○).

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REFERENCES

1. T. Nakata, T. Otsu, and M. Imoto, *J. Polymer Sci.*, **A3**, 3383 (1965).
2. T. Nakata, Y. Kinoshita, T. Otsu, and M. Imoto, *Kogyo Kagaku Zasshi*, **68**, 864 (1965).
3. T. Nakata, T. Otsu, and M. Imoto, *J. Macromol. Chem.*, **1**, 553 (1966).
4. T. Nakata, T. Otsu, and M. Imoto, *J. Macromol. Chem.*, **1**, 563 (1966).
5. T. Nakata, *Kogyo Kagaku Zasshi*, **65**, 1044 (1962).
6. F. A. Bovey and G. V. D. Tiers, *J. Polymer Sci.*, **44**, 173 (1960).
7. W. E. Goode, F. H. Owens, R. P. Fellmann, W. H. Snyder, and J. E. Moore, *J. Polymer Sci.*, **46**, 173 (1960).
8. B. Baysal and A. V. Tobolsky, *J. Polymer Sci.*, **9**, 171 (1952).
9. T. Otsu, M. Yamaguchi, T. Nakata, and M. Imoto, *J. Macromol. Sci.*, **A1**, 1457 (1967).
10. T. G. Fox and H. W. Schnecko, *Polymer*, **3**, 575 (1962).
11. T. Otsu, B. Yamada, and M. Imoto, *J. Macromol. Chem.*, **1**, 61 (1966).

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Zusammenfassung

Bei Verwendung von Nickelperoxyd als Initiator der methyl methacrylsäure-polymerisation ergab sich, dass die Radikalpolymerisation leichter vor sich geht als die von Styrol unter vergleichbaren Bedingungen. Ausserdem waren die bei tiefen Temperaturen erhaltenen Polymeren dadurch charakterisiert, dass sie eine etwas erhöhte syndiotaktische Anordnung aufwiesen als normale Radikalpolymere. Aus NMR Messungen der mit Nickelperoxyd erzeugten Polymeren, die bei verschiedenen Temperaturen ausgeführt wurden, ergab sich eine Bestätigung der Bovey-Tier'schen Beziehung, wonach die Wahrscheinlichkeit der Bildung von isotaktischen, syndiotaktischen und heterotaktischen Monomerentriaden innerhalb der Polymerenkette durch einen einzigen Parameter bestimmt ist, nämlich der Wahrscheinlichkeit der isotaktischen Addition des Monomeren im Kettenfortpflanzungsprozess. Das Verhältnis der Geschwindigkeitskonstanten, k_i/k_s, der isotaktischen und syndiotaktischen Addition während der Polymerisation durch Nickelperoxyd konnte in Form folgender Gleichung ausgedrückt werden:

$$k_i/k_s = 1.31 \exp(-1.17 \text{ kcal}/RT)$$

In dieser Gleichung sind die Unterschiede in der Aktivierungsenergie und der Entropie etwas grösser als im Falle gewöhnlicher Radikalpolymerisationen. Diese Verhalten lässt sich erklären, wenn man annimmt, dass das am festen Nickelperoxyd adsorbierte Monomere bevorzugt syndiotaktisch reagiert.

Résumé

On a trouvé que la polymérisation du méthacrylate de méthyl procède plus facilement que la polymérisation du styrène, lorsqu'on emploi le peroxyde de nickel comme initiateur de polymérisation. Les polymères obtenus à basses températures possèdent une séquence syndiotactique un peu augmentee en comparaison avec les polymères radicalaires ordinaires. On a confirmé à l'aide des déterminations de RNM des polymères obtenus avec le peroxyde de nickel, que la rélation de Bovey-Tiers sur les probabilités de formation de triades d'unités de monomères isotactiques, syndiotactiques et hétérotactiques, etant controlées par un seul paramètre de probabilité d'addition isotactique dans le stade de propagation, est valable dans ce cas. D'une maniére analogue le rapport (k_i/k_s) des constantes de vitesse des additions isotactiques et syndiotactiques dans la polymérisation en masse avec le peroxyde de nickel, est exprimé par l'équation suivante:

$$k_i/k_s = 1.31 \exp(-1.17 \text{ kcal}/RT)$$

Dans cette équation les différences d'énergie d'activation et d'enthropie sont un peu plus grandes que celles rapportées pour une polymérisation radicalaire ordinaire. Si le monomère adsorbé sur le peroxyde de nickel solide est favorisé pour entrer dans la propagation syndiotactique, ces résultats deviendront comprehénsibles.

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