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Polymerization of Methyl Methacrylate under Ultrasonic Irradiation. Part II. Polymerization in Toluene–Dimethyl Sulfoxide Mixed Solvent

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Synopsis

Polymerization of methyl methacrylate with Grignard reagents in mixed solvent of toluene and dimethyl sulfoxide (DMSO) under ultrasonic irradiation was carried out, and the effects of ultrasonic irradiation in connection with the mixed solvent on the stereoregularity and the properties of the polymers obtained were studied. The yield of polymers decreases with increasing concentration of DMSO in the solvent, and both yield and intrinsic viscosity of the polymers produced under ultrasonic irradiation are lower than those of polymers produced without it. A marked change in the configurational structure, namely, decrease in isotactic structure, is observed at a DMSO: toluene volume ratio of 5:95 in the series without ultrasonic irradiation, while a higher concentration of DMSO 15% by volume is required to obtain similar results in the series with ultrasonic irradiation.

Introduction

In the previous paper of this series[1], an attempt was made to obtain some information on the microstructure in the transition state of the polymerization of methyl methacrylate. It was reported that ultrasonic irradiation did not affect the stereoregularity of the polymers but gave lower yield and lower intrinsic viscosity of the polymers produced than without ultrasonic irradiation if polymerization was carried out in a nonpolar solvent such as toluene. Thus we assumed that the proposed bonds between active polymer end and the gegenion are fairly strong in nonpolar solvent. In this experiment, the effect of ultrasonic irradiation in connection with the polarity of solvent on the stereoregularity and the properties of the polymers was studied.

Experimental

Methyl methacrylate was purified by vacuum distillation under nitrogen after removal of water by sodium sulfate. Grignard reagent (phenylmagnesium bromide) was prepared as described previously.[1] Polymerization with Grignard reagent in a mixed solvent of DMSO and toluene was carried out at 15°C. for 30 min.; parallel runs were carried out without ultrasonic irradiation. The ultrasonic generator was the same as that previously

used. Termination was carried out with methanol containing a small amount of hydrochloric acid. Determination of the structure of the polymers was made by both infrared and NMR spectral analysis.[2-5]

Results and Discussion

The yield of the methanol-insoluble polymer is shown in Table I. The intrinsic viscosity of the polymers is shown in Table II. It is clear that both the yield of methanol-insoluble material and the intrinsic viscosity of the polymers produced with ultrasonic irradiation are lower than those of polymers produced without it. In addition, the yield decreases with increasing concentration of DMSO in the mixed solvent, and a marked decrease is observed at a DMSO:toluene ratio of about 5:95. The intrinsic viscosity of the polymers also decreases with increasing concentration of dimethyl sulfoxide. The results mentioned above are more clearly confirmed when one plots the yield and intrinsic viscosity against the concentration of dimethyl sulfoxide in the mixed solvent (Figs. 1 and 2).

TABLE I
Yield of Poly(methyl Methacrylate)[a]

With ultrasonic irradiation			Without ultrasonic irradiation		
Expt. no.	DMSO:-toluene (vol.)	Yield, %	Expt. no.	DMSO:-toluene (vol.)	Yield, %
1	0:100	44.9	2	0:100	54.6
3	0.5:99.5	31.9	4	0.5:99.5	55.3
5	1:99	29.8	6	1:99	—
7	3:97	18.7	8	3:97	19.4
9	5:95	4.7	10	5:95	11.1
11	10:90	3.1	12	10:90	9.8
13	15:85	1.5	14	15:85	4.7
15	20:80	0.5	16	20:80	2.5
17	100:0	0.1	18	100:0	2.0

[a] Polymerization: 4 ml. monomer, 16 ml. toluene, 3 ml. initiator (phenylmagnesium bromide).

TABLE II
Intrinsic Viscosity

With ultrasonic irradiation		Without ultrasonic irradiation	
Expt. no.	$[\eta]$, dl./g.	Expt. no.	$[\eta]$, dl./g.
1	0.91	2	1.13
3	1.35	4	2.20
5	1.32	6	2.10
7	1.16	8	1.75
9	1.03	10	1.52
11	0.75	12	1.46
13	0.71	14	1.26

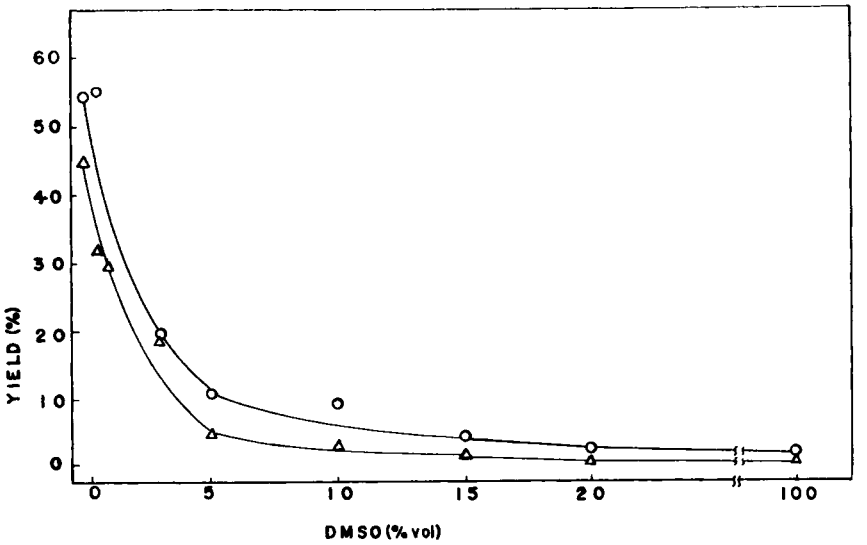

Fig. 1. Yield of poly(methyl methacrylate): (○) without ultrasonic irradiation; (△) with ultrasonic irradiation.

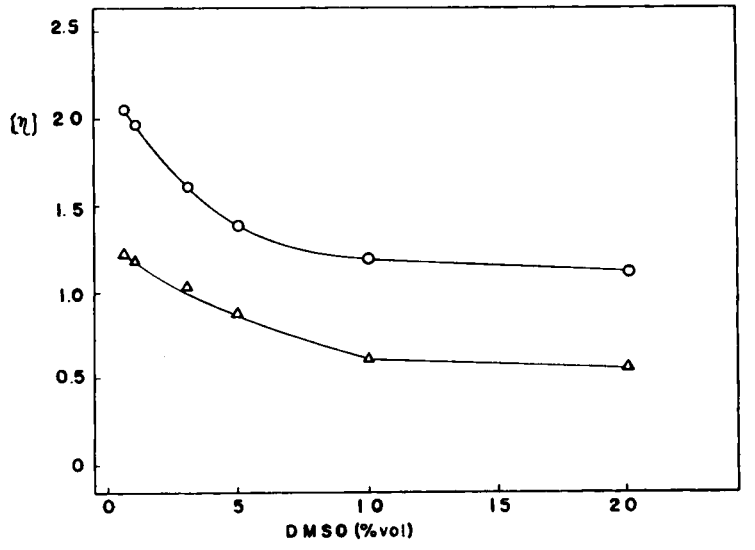

Fig. 2. Intrinsic viscosity of poly(methyl methacrylate): (○) without ultrasonic irradiation: (△) with ultrasonic irradiation.

The structure of the polymers was determined by both infrared and NMR spectral analysis. In infrared spectral analysis, the J value, which is a parameter of stereospecificity of the polymer, was determined according to Goode et al.[2] In NMR spectral analysis, relative amounts of isotactic syndiotactic and atactic structure were determined.[3–5] The results obtained are shown in Table III.

TABLE III
Configurational Structure of the Polymers

With ultrasonic irradiation					Without ultrasonic irradiation				
			NMR					NMR	
Expt. no.	Infrared *J* value	Isotactic, %	Syndiotactic, %	Heterotactic, %	Expt. no.	Infrared *J* value	Isotactic, %	Syndiotactic, %	Heterotactic, %
1	28	97.7	2.0	0.5	2	31	97.3	2.2	0.5
3	26	97.6	0.8	1.6	4	27	97.6	0.7	1.7
5	27	97.3	0.6	2.1	6	25	97.2	1.3	1.5
7	29	89.2	4.8	6.0	8	30	90.2	3.4	6.4
9	27	90.4	4.7	4.9	10	51[a]	57.8	22.0	20.2
11	27	89.6	4.2	6.2	12	58[a]	56.2	24.9	18.9
13	73[a]	48.0	32.3	19.7	14	79[a]	48.5	32.9	18.6
15	76[a]	47.5	32.3	20.2	16	101[b]	42.7	29.5	27.8
17	114[b]	—	—	—	18	110[b]	5.1	49.2	45.7

[a] Isotactic syndiotactic type.
[b] Syndiotactic type.

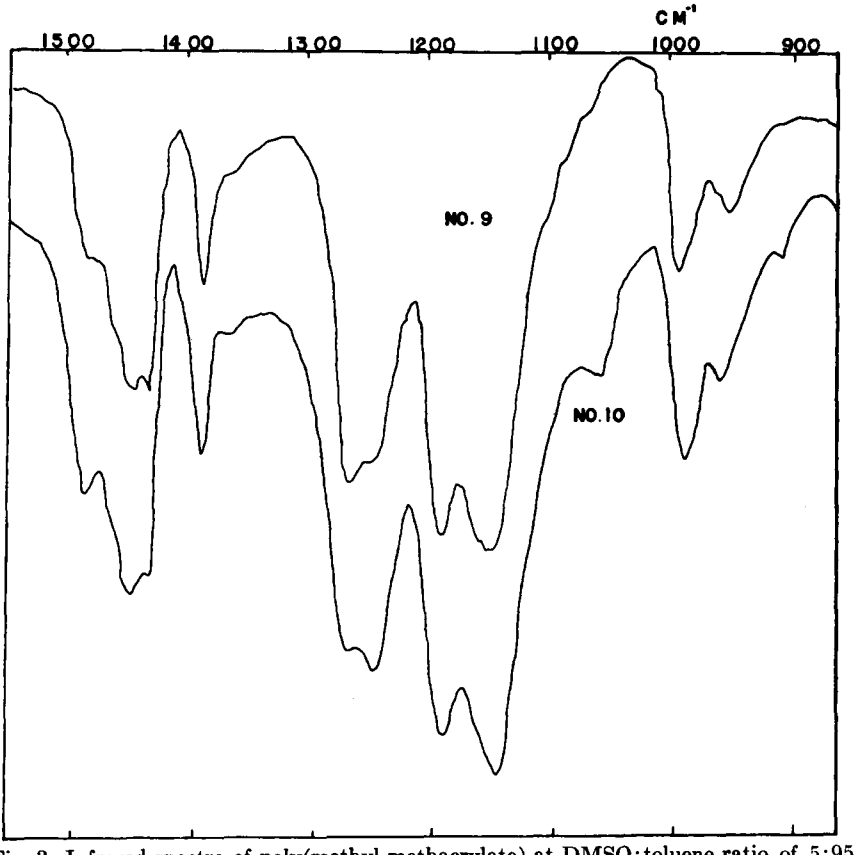

Fig. 3. Infrared spectra of poly(methyl methacrylate) at DMSO:toluene ratio of 5:95 (*9*) with ultrasonic irradiation; (*10*) without ultrasonic irradiation.

It is well known that the polarity of the solvent affects the stereoregularity of the polymers and polar solvent gives a polymer with less isotactic structure.[6] The experimental results also demonstrate this. As shown in Table III, isotactic structure decreases with increasing concentration of dimethyl sulfoxide, and a striking change in the configurational structure of the polymers is observed in a certain limited region. The striking change occurs at a DMSO:toluene ratio of 5:95 without ultrasonic irradiation; on the other hand in the series with ultrasonic irradiation the similar phenomena are observed at a DMSO:toluene ratio of about 15:85. Typical infrared and NMR spectra are shown in Figures 3 and 4.

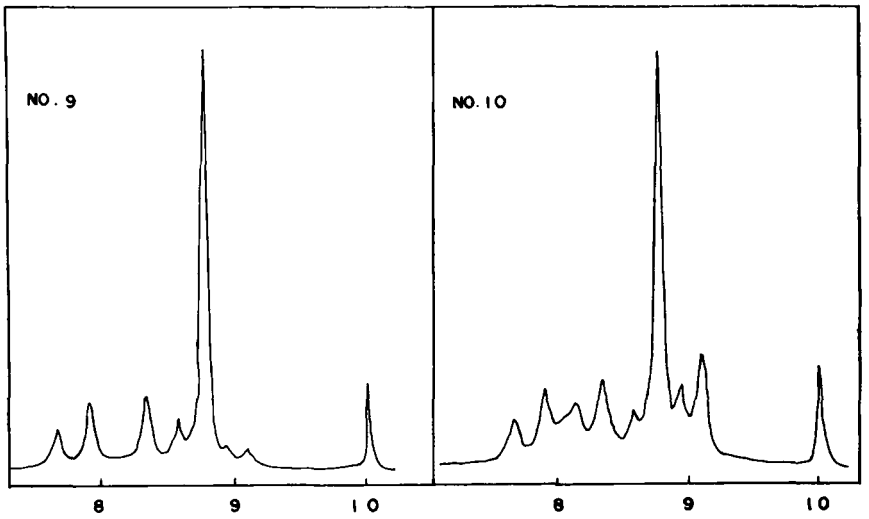

Fig. 4. NMR spectra of poly(methyl methacrylate) at a DMSO:toluene ratio of 5:95: (*9*) with ultrasonic irradiation; (*10*) without ultrasonic irradiation.

It is of interest to observe the higher concentration of dimethyl sulfoxide necessary in the series with ultrasonic irradiation than without it to obtain a polymer with less isotactic structure. In the previous experiment, in which toluene was used as a nonpolar solvent, it was demonstrated that a contact ion-pair between a growing polymer end and catalyst gegenion is fairly strong and is not affected by externally supplied energy such as that of an ultrasonic wave of 500 kc./sec. In these experiments, it was assumed that the bonds between the growing polymer end and gegenion are presumably weakened by solvation of the ion-pair in the transition state of the polymerization, and a change in stereoregularity at lower dimethyl sulfoxide concentration with ultrasonic irradiation than without ultrasonic irradiation was expected. However, the results in the present experiments in conjunction with the previous ones suggest that the ion-pair is not affected by the externally supplied energy such as that of an ultrasonic wave of 500 kc./sec. but in a limited concentration of dimethyl sulfoxide in

mixed solvent the solvated state formed between catalyst gegenion and polar solvent seems to be affected by the ultrasonic irradiation. The fact that a higher concentration of dimethyl sulfoxide is necessary in the series with ultrasonic irradiation than without it to obtain a polymer with less isotactic structure may give helpful information for the understanding of the fine structure of the transition state of the polymerization.

At present the following tentative assumption for the interpretation of the results mentioned above is made. In a limited concentration of polar solvent such as dimethyl sulfoxide in mixed solvent, the reacting site is surrounded by polar solvent to produce a rather heterogeneous state of mixed solvent without ultrasonic irradiation, while the heterogeneous state is homogenized by ultrasonic irradiation, and a regulated monomer approach to a growing polymer end is preferred to a random approach. At higher concentration of dimethyl sulfoxide, the effect of the ultrasonic wave on the stereoregularity of the polymer is no longer observed, since the solvating power of the solvent with respect to the reacting site is reasonably increased. Further investigation is necessary to confirm the above supposition.

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Résumé

La polymérisation du méthacrylate de méthyle au moyen de réactif de Grignard dans des solvants mixtes toluène et diméthylsulfoxyde (DMSO) sous irradiation au moyen d'ultrasons a été effectuée, et les effets de l'irradiation ultrasonique en rapport avec le solvant mixte sur la stéréorégularité et les propriétés des polymères obtenus ont été étudiés. Le rendement en polymère décroît avec une augmentation de la concentration en DMSO dans le solvant, et, à la fois, le rendement et la viscosité intrinsèque des polymères, produits sous irradiation ultrasonique, étaient plus faibles que ceux des polymères produits en absence de ceux-ci. Une modification notable de la structure configurationnelle à savoir une diminution de structure isotactique était observée pour un rapport en volume 5:95 (DMSO/toluène) dans la série sans irradiation ultrasonique, tandis qu'une concentration plus élevée de DMSO, á savoir de 15% en volume est nécéssaire pour obtenir des résultats semblables dans des séries dans lesquelles l'irradiation ultrasonique était utilisée.

Zusammenfassung

Die Polymerisation von Methylmethacrylat wurde mit Grignard-Verbindungen in einem Lösungsmittelgemisch aus Toluol und Dimethylsulfoxyd (DMSO) mit Ultraschallbestrahlung ausgeführt und der Einfluss der Ultraschallbestrahlung gemeinsam mit dem des Mischlösungsmittels auf die Steroregularität und die Eigenschaften der erhaltenen Polymeren untersucht. Die Polymerausbeute nimmt mit steigender DMSO-Konzentration im Lösungsmittel ab und Ausbeute sowie Viskositätszahl der bei Ultraschallbestrahlung gebildeten Polymeren sind niedriger als ohne Einwirkung von Ultraschall. Bei der Reihe ohne Ultraschallbestrahlung wird bei einem Volumsverhältnis 5:95 (DMSO:Toluol) eine merkliche Konfigurationsänderung, nämlich eine Abnahme der isotaktischen Struktur beobachtet, während zur Erreichung ähnlicher Ergebnisse in der Reihe mit Ultraschallbestrahlung eine höhere DMSO-Konzentration, 15 Volums %, erforderlich ist.

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