

Polymerization of Methyl Methacrylate under Ultrasonic Irradiation

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Synopsis

Polymerization of methyl methacrylate with Grignard reagents and benzoyl peroxide under ultrasonic irradiation was carried out and the effect of the ultrasonic irradiation on the stereoregularity and the properties of the polymers obtained was studied. No effect of ultrasonic irradiation on the stereoregularity of the polymers was observed, but the yield and the intrinsic viscosity of the polymers were lower than those of polymers produced without ultrasonic irradiation. It is, therefore, assumed that the bonds at a propagating site between an active polymer end and a counterion are fairly strong and are not broken by the externally applied energy corresponding to an ultrasonic wave of 500 kcycles/sec., even though carbon-carbon covalent bonds in the main chain are broken.

Introduction

Since Natta's school successfully prepared polypropylene of high stereoregularity, a large number of studies concerning stereospecific polymerization have been carried out by many researchers. At present, one of the most significant problems in this field seems to be the study of the detailed mechanism of stereospecific polymerization. Although one may first consider whether polymerization proceeds through a free ion or an ion-pair, ion-pair theory is mostly accepted for the formation of polymers with isotactic structure. Cram and Kopecky,¹ Higashimura,² and Bawn and Ledwith³ insist that a growing polymer does not assume the planar structure in the sp^2 orbital but bonds with a counterion in the sp^3 orbital. Recently, Schuerch et al.⁴ and Yoshino et al.⁵ studied the stereoregularity of poly(isopropyl α , *cis*- β - d_2 -acrylate) and poly(methyl α , β - d_2 -acrylate), respectively, and discussed the mechanism of the opening of the double bond in the approaching monomer.

We assumed that if polymerization of a vinyl monomer were carried out under a special condition which might affect the fine structure of the propagating site, namely proposed bonds between a growing polymer end and the catalyst counterion, there would be some change in stereoregularity

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of the polymer, and the resulting information would be helpful for the understanding of the detailed mechanism of the polymerization. For the experimental approach, polymerization of methyl methacrylate was carried out under ultrasonic irradiation.

Experimental and Results

Methyl methacrylate was purified by vacuum distillation under nitrogen after removal of water by sodium sulfate. Grignard reagent (phenylmagnesium bromide) was prepared from 6.1 g. of magnesium and 26.2 ml. of phenyl bromide in ether. Ether was replaced with 120 ml. of toluene by distillation of ether.

Polymerization with Grignard reagent in toluene was carried out at 15°C. for periods of time ranging from 15 to 300 min.; parallel runs were carried out with and without ultrasonic irradiation. Polymerization with benzoyl peroxide (BPO) was carried out in the same way at 70°C. for 300 min. only. A specially constructed ultrasonic generator and a push-pull

TABLE I
Yields of Poly(methyl Methacrylate)^a

With ultrasonic irradiation				Without ultrasonic irradiation			
Expt. no.	Time, min.	Initiator	Yield, %	Expt. no.	Time, min.	Initiator	Yield, %
1	210	BPO	74.1	2	210	BPO	76.0
3	15	Grignard reagent	42.6	4	15	Grignard reagent	47.8
5	30	"	44.1	6	30	"	51.8
7	60	"	49.1	8	60	"	69.4
9	180	"	41.7	10	180	"	53.5
11	300	"	51.9	12	300	"	67.6

^a For the runs with the Grignard reagent (phenylmagnesium bromide), 4 ml. monomer, 16 ml. toluene, and 3 ml. initiator were used; for the runs with benzoyl peroxide, 5 ml. monomer, 5 ml. toluene, and 100 mg. initiator were used.

oscillator energizing a ceramic crystal of 6 cm. diameter were used to generate ultrasonic waves of a frequency of 500 kcycles/sec.* Termination was carried out with methanol containing a small amount of mineral acid. (In the case of ultrasonic irradiation this treatment was made during treatment.) Purification of the polymer was carried out by precipitation with the chloroform-methanol solvent system as usual.

The yields of poly(methyl methacrylate) are shown in Table I. In all cases for paired runs, the yields were greater in the absence of ultrasonic irradiation.

The intrinsic viscosities measured in benzene are shown in Table II. The structure of the polymers was determined by both infrared and

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TABLE II
Intrinsic Viscosity of Poly(methyl Methacrylate)

With ultrasonic irradiation		Without ultrasonic irradiation	
Expt. no.	$[\eta]$, 100 ml./g.	Expt. no.	$[\eta]$, 100 ml./g.
1	0.28	2	0.38
3	0.97	4	1.51
5	0.90	6	0.98
7	0.91	8	1.29
9	0.94	10	1.04
11	0.83	12	1.60

NMR spectral analysis.⁶⁻⁹ The NMR instrument was from Japan Electron Optics, C-60 type. The results are shown in Table III.

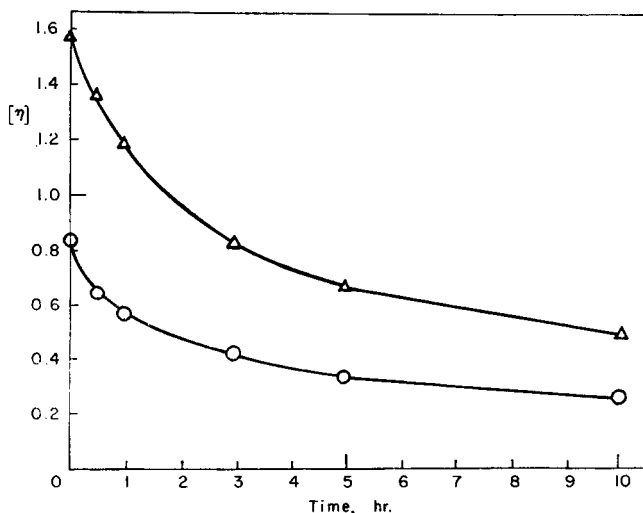


Fig. 1. Degradation of poly(methyl methacrylate) by ultrasonic irradiation: (Δ) isotactic; (\circ) syndiotactic.

Furthermore ultrasonic treatment of the polymers prepared with Grignard reagent (No. 12) and with γ -ray irradiation was carried out in benzene at a concentration of 0.75% at 15°C. in order to determine if the degradation of polymer occurs on ultrasonic irradiation. The results are shown in Figure 1.

Discussion

As shown in Table I, the yield of the methanol-insoluble polymer was obviously affected by the ultrasonic irradiation. In the case of ultrasonic-irradiated sample the yield was always lower than that of polymer prepared without ultrasonic treatment. Analogous results were observed in the case

TABLE III
Structure of Poly(methyl Methacrylate)

Expt. no.	J value ^a	With ultrasonic irradiation			Without ultrasonic irradiation				
		Isotactic, %	Syndiotactic, %	Atactic, %	Expt. no.	J value	Isotactic, %	Syndiotactic, %	Atactic, %
1	104	5.6	62.4	32.0	2	101	5.9	59.5	34.6
3	29	92.2	6.3	1.5	4	34	97.3	2.2	0.5
5	28	97.7	2.0	0.3	6	31	—	—	—
7	27	95.2	4.4	0.4	8	33	—	—	—
9	29	95.7	3.5	0.8	10	27	—	—	—
11	28	95.8	3.5	0.7	12	28	97.0	2.5	0.5

^a A J value of 25-35 denotes isotactic structure; a J value of 100-115 is indicative of syndiotactic structure.

of intrinsic viscosity (Table II). It is, therefore, assumed that degradation of polymer occurred during the ultrasonic irradiation. As shown in Figure 1, the intrinsic viscosity of both polymers dropped markedly on ultrasonic irradiation. Some studies on this problem have already been reported,¹⁰⁻¹² and we are studying the phenomenon in some detail.

The results shown in Table III indicate that the polymers polymerized with Grignard reagent were predominantly isotactic in structure, while those polymerized with benzoyl peroxide had a syndiotactic structure. These results were also confirmed by NMR spectral analysis (Table III). The results of the structural analysis of the polymers by both infrared and NMR spectra suggest that the ultrasonic wave irradiation did not affect the stereoregularity of the polymers.

If it is supposed that the propagation proceeds through ion-pair theory, bonds must exist between a growing active polymer end and counterion, and monomer approaches to the reacting site by some modes. No experiments on the strength of these bonds have been made, but one would assume that these bonds are less strong than the carbon-carbon covalent bonds in the main chain. However, the present experiments did not prove this assumption; therefore, the results above are presumably good evidence that in the transition state in polymerization a growing polymer end and catalyst form rather strong bonds which cannot be broken by the externally applied energy corresponding to an ultrasonic wave of 500 keycles/sec., and the configurational structure of the irradiated polymer is the same as that of the conventional polymer.

Furthermore, lower yield and lower intrinsic viscosity were observed in the ultrasonic irradiated polymers. In addition, obvious degradation of the polymer by the ultrasonic irradiation was observed. These results seem to be helpful for understanding the detailed mechanism of the stereospecific polymerization, if it is recalled that the polarity of the solvent does affect the stereoregularity of polymers.¹³

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Résumé

On a effectué la polymérisation du méthacrylate de méthyle avec le réactif de Grignard et le peroxyde de benzoyle sous irradiation aux ultrasons et on a étudié l'influence de l'irradiation aux ultrasons sur la stéréorégularité et les propriétés des polymères obtenus. On n'a pas observé d'influence de l'irradiation aux ultrasons sur la stéréorégularité des polymères; mais le rendement et la viscosité intrinsèque de ces polymères était plus faibles que ceux qui ont été polymérisés en absence d'ultrasons. Ainsi, on admet que les liaisons d'un lien de propagation situé entre une fin de polymère actif et un contre-ion sont assez fortes, et ne sont pas rompues par l'énergie extérieure, correspondant à une onde ultrasonique de 500 Kc/sec bien que les liaisons covalentes carbone-carbone dans la chaîne principale sont cassées.

Zusammenfassung

Die Polymerisation von Methylmethacrylat wurde mit Grignard-Reagentien und Benzoylperoxyd unter Einwirkung von Ultraschall durchgeführt und der Einfluss des Ultraschalls auf die Eigenschaften der erhaltenen Polymeren untersucht. Es wurde kein Einfluss des Ultraschalls auf die Stereoregularität der Polymeren beobachtet, es waren aber Ausbeute und Viskositätszahl der Polymeren niedriger als bei Polymerisation ohne Ultraschall. Es wird daher angenommen, dass die Bindungen zwischen einem aktiven Polymerende und einem Gegenion am Wachstumsort ziemlich fest sind und durch die äusserlich angewandte, einer Ultraschallwelle von 500 Khz entsprechende Energie nicht gesprengt werden, obgleich kovalente Kohlenstoff-Kohlenstoffbindungen in der Hauptkette gesprengt werden.

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