SHORT COMMUNICATIONS

Pronounced Effects of Temperature and Monomer Concentration on Isotactic Specificity of Triphenylmethyl Methacrylate Polymerization through Free Radical Mechanism. Thermodynamic *versus* Kinetic Control of Propagation Stereochemistry

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The stereochemical control of free radical reaction is generally more difficult than that of the other types of reactions.¹ This is the case not only for the organic synthesis but also for macromolecular chemistry; only few examples are known as stereoregular free radical polymerization in solution.^{2–5} Further, the stereospecificity of free radical polymerization in solution relies mainly on the structure of starting monomer, which makes it difficult to obtain polymers with widely varying stereoregularity from a certain monomer.

In the present study, we found remarkable effects of reaction temperature, monomer concentration in feed ($[M]_0$), and solvent on tacticity in the free radical polymerization of triphenylmethyl methacrylate (TrMA) and succeeded in the synthesis of the polymers having triad isotacticity (mm) ranging from 64% to 99%.^{6–8} This communication describes the stereochemistry of TrMA polymerization in comparison with that of the polymerizations of methyl methacrylate (MMA) and 1-phenyldibenzosuberyl methacrylate (PDBSMA), a TrMA analogue, which we have reported to give a highly isotactic polymer by radical polymerization.³ TrMA is known to give an isotactic polymer by radical polymerization though the triad isotacticity has been reported to be only 64%.² The isospecificity in this polymerization can be ascribed to a helical conformation of the growing radical because TrMA leads to an optically active, almost perfectly isotactic, and purely single-handed helical polymer by asymmetric anionic polymerization^{9–11} as well as the other bulky methacrylates.¹²

The conditions and results of polymerization of TrMA, PDBSMA, and MMA in toluene are summarized in Table I. It can roughly be said that a lower temperature and a higher $[M]_0$ give a higher yield and a higher degree

of polymerization (DP) of the products in the polymerizations of the three monomers. A higher propagation rate at a higher $[M]_0$ and lower chances of depolymerization at a lower temperature may be responsible for these observations.

The polymers having the wide range of tacticity were obtained by changing reaction temperature and $[M]_0$ in TrMA polymerization. At a higher polymerization temperature and at a lower $[M]_0$, a higher isotacticity was achieved; the mm content of the polymer exceeded 98% under the conditions of runs 4 and 7 (Figure 1). In contrast to the TrMA polymerization, almost perfectly isotactic polymers were obtained regardless of $[M]_0$ and temperature in the polymerization of PDBSMA (runs 8–11)¹³ and the stereochemistry of MMA polymerization was not affected by $[M]_0$ (runs 12–14). Reaction temperature is known to affect stereochemistry of MMA polymerization to a small extent; rr triad content decreases only by 5% with increasing reaction temperature from 30°C to 70°C.¹⁴

We propose the following models of propagating species in order to understand the unusual results. (1) There are, at least, two types of helical propagating radicals having different possibilities of meso monomer addition. (2) The two may differ from each other in the conformation in the vicinity of the ω -end radical. (3) The one of the two having a lower possibility of meso monomer addition is formed on monomer addition and is thermodynamically less stable than the other having a higher possibility of meso monomer addition; the latter is yielded from the former through stereomutation taking place at a rate of a comparable order to that of the propagation rate.¹⁵ These assumptions well explain the higher meso specificity at a higher temperature and at a lower $[M]_0$ where the stereomutation between the two radicals can be faster compared to propagation. In other words, *at a higher temperature and a lower $[M]_0$, the reaction is mediated predominantly by the more stable growing radical (thermodynamic control) and under the reversed conditions, predominantly by the less stable growing radical formed on monomer addition (kinetic control).*

The helical structure of propagating radicals in the PDBSMA polymerization may be too rigid to take the two structures assumed for the TrMA polymerization and only one leading to meso monomer addition may

Table I. Free radical polymerization of TrMA, PDBSMA, and MMA in toluene under various conditions^a

Run	Monomer	Temp/°C	[M] ₀ /mol·l ⁻¹	Yield ^b /%	DP ^c	Tacticity ^d
						mm/mr/rr
1	TrMA	30	0.18	87.7	227	69.9/20.2/ 9.9
2	TrMA	40	0.18	60.7	130	81.7/13.4/ 4.9
3	TrMA	60	0.18	40.4	122	93.4/ 5.2/ 1.4
4 ^e	TrMA	70	0.18	3.3	102	98.1/ 1.6/ 0.3
5	TrMA	60	0.95	95.8	415	63.6/24.1/12.3
6	TrMA	60	0.34	69.7	244	82.6/13.1/ 4.3
7	TrMA	60	0.12	13.6	135	98.2/ 1.7/ 0.1
8	PDBSMA	30	0.17	88.4	554	99.7/ 0.3/ ~0
9	PDBSMA	40	0.17	87.8	361	99.8/ 0.2/ ~0
10	PDBSMA	60	0.17	75.9	337	99.9/ 0.1/ ~0
11	PDBSMA	60	0.40	89.4	505	99.5/ 0.3/ 0.2
12	MMA	40	6.3	92.6	376	2.5/30.8/66.7
13	MMA	40	0.82	69.1	99	2.5/31.3/66.2
14	MMA	40	0.23	49.4	77	2.6/31.0/66.4

^a Polymerization was carried out in a glass ampoule under N₂ atmosphere. Reaction conditions: [monomer]/[initiator] = 50; monomer 0.5 g; time 144 h (run 1), 24 h (runs 2, 3, 5–14), 6 h (run 4); initiator (iso-PrOCOO)₂ (runs 1, 2, 8, 9, 12–14), α,α' -azobisisobutyronitrile (runs 3–7, 10, 11). The products precipitated out in the polymerizations of runs 1–11. $\bar{M}_w/\bar{M}_n$ of the polymers was in the range of 1.4–5.8 except for run 4; the polymer obtained in run 4 had a $\bar{M}_w/\bar{M}_n$ of 1.27. The reason for this narrow $\bar{M}_w/\bar{M}_n$ is not immediately known. ^b Hexane-insoluble part of the product. ^c Determined by GPC analysis of PMMA derived from the original polymer using polystyrene standard samples. ^d Determined by ¹H NMR analysis of PMMA derived from the original polymer. ^e Polymerization at 80°C under the same conditions as those for run 4 did not result in a sufficient yield of polymer.

Figure 1. ¹H NMR spectra of PMMA derived from poly(TrMA) of run 7 [500 MHz, CDCl₃, 60°C]. c, x, and * denote ¹³C satellite bands, impurity peaks, and the peaks based on the α -methyl groups in the vicinity of the chain terminals, respectively.

be possible. The growing species in MMA polymerization is considered to have only the thermodynamically stable conformation under the current conditions and therefore the polymerization stereochemistry is not obviously affected by temperature and [M]₀.

Solvent also affected reaction stereochemistry: the polymerization of TrMA in tetrahydrofuran under the same conditions as those for run 3 gave a polymer with a triad tacticity distribution of mm/mr/rr = 99.1/0.9/~0 in a yield of 3.3%. This suggests that solvent affects the structure of the growing species.

In conclusion, we described the effects of temperature, [M]₀, and solvent on the stereochemistry of the radical polymerization of TrMA. The current results contain, to the best of our knowledge, the most remarkable influence of the reaction conditions on the stereochemistry of radical reaction in solution. Efforts are underway to learn the applicability of our models¹⁶ to other radical reaction systems and to know the detailed structure of the radical species.

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 13. We reported the mm contents of poly(PDBSMA)s obtained under the conditions identical to those of run 8, 9, and 10 to be 97%, 98%, and 93%, respectively,³ but in the repeated experiments we found the polymers with higher isotacticity are obtained with a high reproducibility. The lower mm contents in the previous study can be ascribed to contaminants in the monomer such as methacrylic acid. Evidentially, the copolymerization of PDBSMA with 2 mol% of methacrylic acid under the reaction conditions of run 10 gave a polymer having a triad tacticity of $mm/mr/rr=95.8/2.9/1.3$ and the copolymerization of TrMA with a 1 mol% of methacrylic acid under the reaction conditions of run 3 resulted in a triad tacticity of $mm/mr/rr=88.0/9.0/3.0$.
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