Macromolecules **1999,** *32,* 1711−1713

Development of a Living Anionic Polymerization of Ethylphenylketene: A Novel Approach to Well-Defined Polyester Synthesis

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Received October 6, 1998
Revised Manuscript Received January 6, 1999

Cummulenes are attractive monomers for synthesizing various functional and reactive polymers having interconversionable functional groups.[1] Recently, several well-designed living polymerizations of cummulenes and their applications have been reported by us[2] and by other groups.[3] Anionic polymerization of ketenes is known to be an useful method for synthesizing polyesters having carbon−carbon double bonds on their side chains;[4] however, detailed study concerning polymerization of ketenes has not been carried out presumably due to the difficulty in controlling their reactions and their lack of facile availability. These circumstances prompted us to develop a living polymerization of ketenes. We focused our attention on alkylarylketenes as monomers in view of diversity in their design and availability. In this paper, we communicate the first example of living polymerization of ethylphenylketene (EPK).[5]

Polymerization of EPK was carried out using butyllithium as an initiator in THF at −20 °C under nitrogen (Scheme 1).[6] When the feed ratio [EPK]/[*n*-BuLi] was 30, the reaction completed within 5 min, and the corresponding polymer was obtained almost quantitatively after precipitation with methanol, of which number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) was estimated to be 5000 and 1.11, respectively (Table 1, entry 1). The structure of poly(EPK) was determined to be polyester on the basis of its strong IR-absorption at 1740 cm^{-1}.[4b] Other organolithium compounds brought about similar results, while other organometals were not effective.[7] When polymerization reactions were carried out at −20 °C with varying the feed ratio [EPK]/[*n*-BuLi], a linear relationship between feed ratio and M_n was observed (Table 1, Figure 1). M_w/M_n was always around 1.1.

The living character of the present polymerization was confirmed by a postpolymerizarion: After the first stage polymerization of EPK (30 equiv to *n*-BuLi) for 20 min at −20 °C, EPK (60 equiv to *n*-BuLi) was fed and allowed to react for an additional 20 min at −20 °C. SEC analysis showed that the unimodal peak of the postpolymer shifted from that of prepolymer toward the higher molecular weight region (Figure 2).

Polymerization at lower temperature (<−40 °C) also afforded the corresponding polymer almost quantitatively; however, the molecular weight distribution broadened (at −40 and at −78 °C, M_w/M_n values were 1.17 and 1.27, respectively). The living character of the polymerization at −78 °C was confirmed by postpolymerization experiment. These results indicate that higher temperature might allow enhancement of relative rate of initiation to propagation enough to accomplish narrow molecular weight distribution. Polymerization at 0 °C also gave poly(EPK) having narrow M_w/M_n (=1.13) almost quantitatively; however, postpolymerizarion was not successful, presumably due to serious termination of the living end at this temperature.

Table 1. Effect of the [EPK]/[*n*-BuLi] Ratio on the Molecular Weight of the Resulting Polymer

run	[EPK]/[*n*-BuLi]	yield/%[a]	M_n[b]	M_w/M_n[b]
1	30	96	5000	1.11
2	60	97	11000	1.10
3	90	98	14900	1.10
4	120	97	21100	1.11

[a] MeOH-insoluble parts. [b] Estimated by SEC (eluent, THF; polystyrene standards).

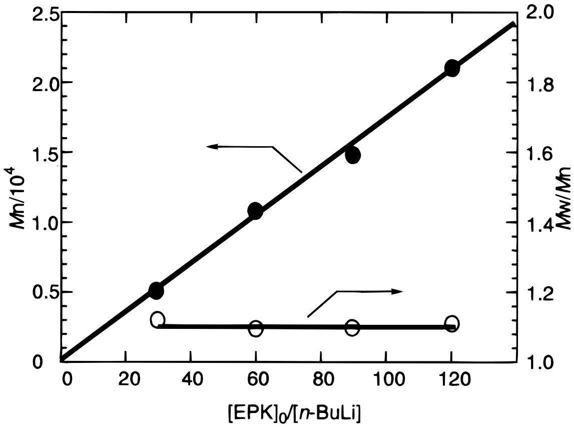


Figure 1. M_n and M_w/M_n vs feed ratio [EPK]/[*n*-BuLi].

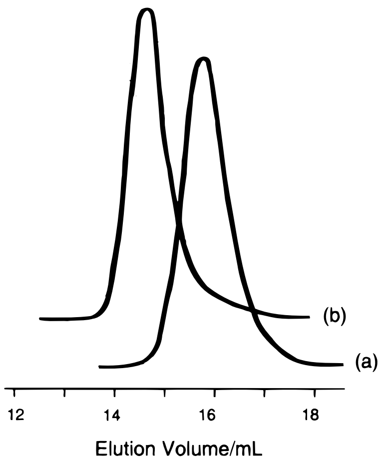
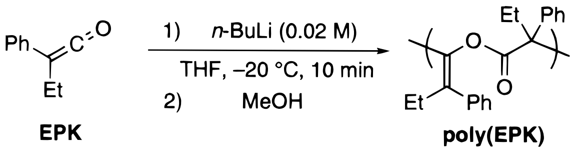


Figure 2. SEC profiles of poly(EPK) in postpolymerization: (a) after prepolymerization of EPK (30 equiv to *n*-BuLi), M_n = 4700 (M_w/M_n = 1.12); (b) after postpolymerization of EPK (60 equiv to *n*-BuLi), M_n = 12 800 (M_w/M_n = 1.13).

Scheme 1



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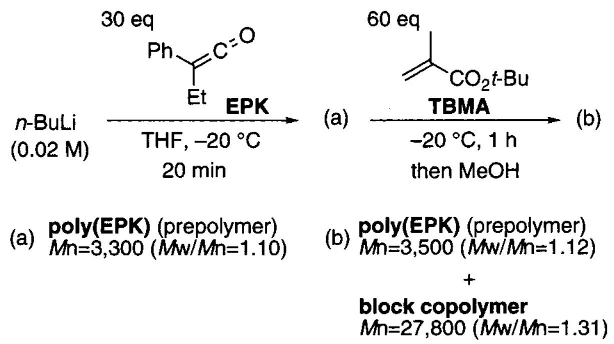
Scheme 2



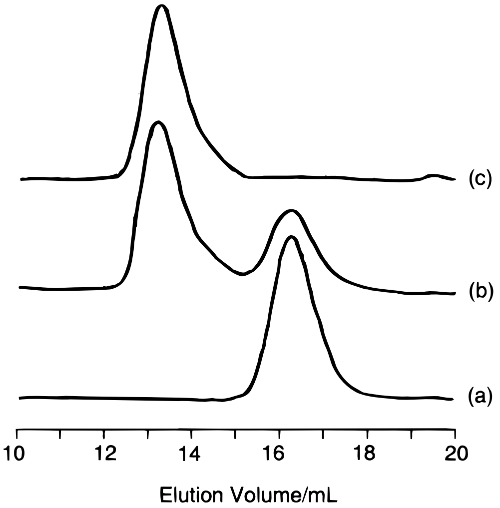


Figure 3. SEC profiles in block copolymerization: (a) after prepolymerization of EPK; (b) after block copolymerimerization; (c) for isolated poly(EPK-*b*-TBMA).

We also examined block copolymerization of EPK with *tert*-butyl methacrylate (TBMA) (Scheme 2): After prepolymerization of EPK (30 equiv to *n*-BuLi) for 20 min at −20 °C, TBMA (60 equiv to *n*-BuLi) was fed and allowed to react for 1 h at −20 °C. An increase in molecular weight was observed in SEC analysis of the obtained mixture, which indicated the formation of the corresponding block copolymer (Figure 3). The peak attributed to the unreacted prepolymer was also detected. It was found that the block copolymer could be separated completely from the prepolymer by thin-layer chromatography using a SiO$_2$ plate with CH$_2$Cl$_2$/hexane (1/1) as an eluent: The block copolymer remains near the spotting point, whereas the prepolymer is quite mobile (R_f = 0.7). ^{1}H NMR spectrum of the isolated block copolymer is shown in Figure 4, in which the signals attributed to the TBMA unit can be found in addition to those attributed to the EPK unit. The block efficiency was estimated to be ca. 35% from the ratio of weight of the block copolymer to that of the remaining prepolymer and from ^{1}H NMR analysis.

It is noteworthy that the remained prepolymer was still alive after the block copolymerization. When EPK (30 equiv to *n*-BuLi) was fed further after the block copolymerization, it was consumed again. In its SEC analysis, the peak of the prepolymer poly(EPK) shifted toward higher molecular weight region ($M_{\rm n}$ = 8400; $M_{\rm w}/M_{\rm n}$ = 1.15), while the peak of the block copolymer did not move. The newly appeared peak is considered to be attributed to the homopolymer of EPK. These results indicate that the low block efficiency in the block copolymerization did not arise from the termination of the living end of poly(EPK) but from a much greater rate of propagation of TBMA than that of initiation under these block copolymerization conditions. Much more effort is required in order to achieve precise block copolymerization.

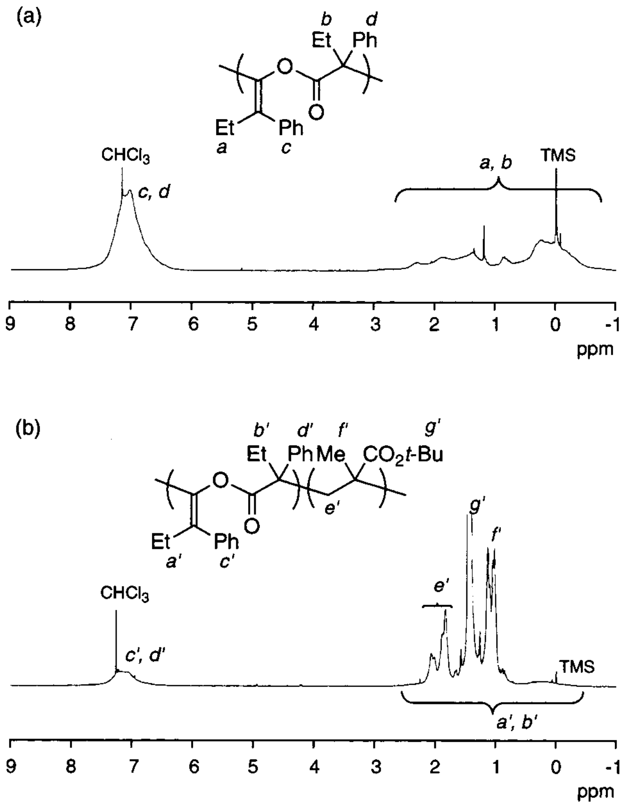


Figure 4. ^{1}H NMR spectra (270 MHz, CDCl$_3$, 55 °C) of the obtained polymers: (a) poly(EPK); (b) isolated poly(EPK-*b*-TBMA).

In summary, the polymerization of ethylphenylketene by *n*-BuLi was found to proceed through a living mechanism. The present polymerization system would provide a novel strategy for synthesis of a polyester with a predictable molecular weight and a narrow molecular weight distribution. Design and polymerization of various functional ketene monomers are now under investigation.

References and Notes

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(5) For the synthesis of EPK, see: Kresze, V. G.; Runge, W.; Ruch, E. *Liebigs Ann. Chem.* **1972**, *756*, 112. For the anionic homopolymerization and copolymerization, see ref 4b.

(6) Representative procedure for the polymerization: Under N$_2$, to a solution of *n*-BuLi (1.52 M in hexane, 66 mL, 0.10 mmol)

in THF (5.0 mL) was added EPK (439 mg, 3.00 mmol) at −20 °C, and it was allowed to react at the same temperature for 10 min. The reaction was quenched by adding MeOH (1 mL), and was poured into MeOH (100 mL). The resultant colorless precipitate was collected by filtration with suction and dried under vacuum to obtain poly(EPK) (440 mg, quantitative): Anal. Calcd for ($C_{20}H_{20}O_2$): C, 82.16; H, 6.89. Found: C, 81.13; H, 7.04.

(7) Polymerization of EPK with sodium naphthalene afforded the corresponding polymer in 70−80% yield, which is in good agreement with that repored.[4b] Its molecular weight distribution was 1.2−1.3 regardless of polymerization temperature (−78 to −40 °C). MeMgBr, $AlMe_3$, and $ZnEt_2$ did not efficiently initiate the polymerization at −78 °C (yield < 10%). The *n*-BuLi + SmI_3 system, which has been reported to be effective in polymerization of isocyanates,[1g] gave poly(EPK) having narrow M_w/M_n (∼1.2) at −20 °C; however, postpolymerization was not successful.

MA981567R