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SHORT COMMUNICATIONS

Molecular Weight Control of Polymer through Radical Chain Polymerization in the Crystalline State

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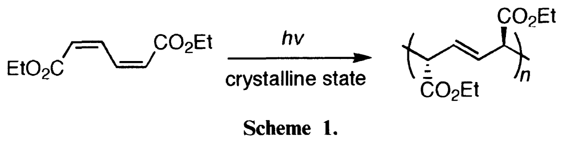
Molecular weight and its distribution are controlled by living polymerization which has been established in anionic, cationic, radical, ring-opening, and metathesis polymerizations.[1,2] Organic synthetic approaches[3-5] and genetic engineering[6] as well as separation using supercritical fluid chromatography[7] provide uniform polymers which have no molecular weight distribution. There have been some attempts to control the molecular weight of a polymer produced in radical chain polymerizations under specific reaction loci. For example, templates were used for the synthesis of oligomers of a specific chain length.[8,9] The possibility of the formation of a monodisperse polymer in an emulsion polymerization system has also been discussed.[10] Recently, Nakanishi and coworkers successfully prepared microcrystals of polydiacetylene derivatives, and they revealed some characteristic features, *e.g.*, excitonic absorption depending on the size of the microcrystals in comparison with that of large bulk crystals.[11] They mentioned the relationship between the crystal size and the chain length of the resulting polymers.[12,13]

In 1994, we discovered a new topochemical polymerization of diethyl (*Z*,*Z*)-muconate (EMU) in the crystalline state by photoirradiation to yield a stereoregular and ultra-high molecular weight polymer (Scheme 1).[14-16] This polymerization proceeds *via* a radical chain mechanism, and the propagation is very fast, resulting in the formation of high molecular weight polymers even at the initial stage of the polymerization, *i.e.*, at a low conversion. The polymerization of the EMU crystals occurs along the specific axis of the crystals to provide polymer crystals in which the polymer chains are aligned in a completely stretched form. The X-ray diffraction of the poly(EMU) crystals revealed that the fiber period is 0.4835 nm, suggesting that we can control the polymer chain length by a change in the crystal size, *i.e.*, the length of the needles as the monomer crystals. For instance, a crystal of EMU with a size of 10^{-6} m would provide a polymer with a degree of polymerization of 2×10^3, that is, a molecular weight of 4×10^5, if there is no defect in the crystal. In this paper, we describe the preliminary results of the molecular weight control of polymers using the features of the crystalline-state polymerization by radical chain reactions.



Scheme 1.

The typical results obtained are summarized in Table I. The recrystallization with *n*-hexane on slow cooling to -20°C gave a considerably large size of crystals, a mixture of 10^{-3} to 10^{-2} m length of the needles. The photopolymerization of the crystals with a high-pressure Hg lamp at 0°C for 4 h provided polymers with an ultrahigh molecular weight in 37% yield, of which the $[\eta]$ value reached $1.94 \times 10^3\,\mathrm{cm^3\,g^{-1}}$ (run 1), as described in the previous papers.[15,16] An attempt at the determination of molecular weight by gel permeation chromatography (GPC) failed because of the exclusion limit of the column used. The recrystallization on rapid cooling to -78°C gave thinner crystals of 10^{-4} to 10^{-3} m in length, but the $[\eta]$ value of the resulting polymer was still as large as $1.35 \times 10^3\,\mathrm{cm^3\,g^{-1}}$ (run 2). The recrystallization with other solvents including acetone, methanol, ethanol, and ethyl acetate resulted in the formation of similar polymers, *i.e.*, the $[\eta]$ values were 1.1—$2.1 \times 10^3\,\mathrm{cm^3\,g^{-1}}$. Second, the large size crystals prepared by the ordinary recrystallization were crushed mechanically. Whereas milling with a porcelain mortar showed no effect on the change in the molecular weight of the polymer (run 3), a ball milling method reduced the $[\eta]$ value of the polymer to $2.0 \times 10^2\,\mathrm{cm^3\,g^{-1}}$ (run 4). The scanning electron microscopy (SEM) observation revealed that the crystal sizes were in a wide range of 10^{-6} to 10^{-4} m for the polymer obtained, indicating that the milling method is not favored for molecular weight control. Subsequently, we attempted control of the crystal growing by the freeze-drying method. When a benzene solution of EMU was frozen in a dry ice-methanol bath and then the benzene was evaporated at 0°C *in vacuo*, followed by photoirradiation at 30°C for 4 h, a polymer with $[\eta]$ of $6.6 \times 10^2\,\mathrm{cm^3\,g^{-1}}$ was produced in 20% yield (run 5). The optical and SEM photographs suggested the formation of small size crystals in the range of 10^{-6}—10^{-5} m, but larger size crystals (10^{-5}—10^{-6} m) also existed simultaneously. The large crystals seemed to be formed in the cooling process. We have found that the microcrystals are also prepared by the precipitation method,[11] *i.e.*, an ethanol solution of EMU (0.04—0.2 $\mathrm{mol\,L^{-1}}$) was added dropwise using a syringe into a large amount of water at room temperature with or without

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Table I. Photopolymerization of EMU crystals prepared by various methods

Run No.	Method of crystal preparation[a]	Crystal size[b]/m	Polymerization conditions[c]	Polymer yield/%	$[\eta]^d \times 10^{-2}$ cm^3 g^{-1}
1	Recrystallization (slow cooling)	10^{-3}—10^{-2}	A	37.2	19.4
2	Recrystallization (rapid cooling)	10^{-4}—10^{-3}	A	23.0	13.5
3	Milling with mortar	10^{-5}—10^{-4}	A	20.4	16.1
4	Ball mill	10^{-6}—10^{-4}	B	12.5	2.0
5	Freeze-drying	10^{-6}—10^{-4}	C	20.0	6.6
6	Precipitation (moderate stirring)	10^{-6}—10^{-5}	D	11.5	0.63[e]
7	Precipitation (vigorous stirring)	10^{-6}—10^{-5}	D	5.0	0.38[f]
8	Precipitation (without stirring)	10^{-6}—10^{-5}	D	11.0	0.80[g]

[a] Recrystallization from *n*-hexane with slow cooling to −20°C or rapid cooling to −78°C. Milling was carried out with a porcelain mortar or using a steel ball with a diameter of 4 mm (milling time 1 min). Freeze-drying was carried out with benzene at 0°C. The solution ([EMU] = 0.2 mol L^{-1}) was cooled with a dry ice-methanol bath. For the precipitation method, ethanol and water were used as the solvent and the non-solvent, respectively. The solution ([EMU] = 0.04—0.20 mol L^{-1}, 50 mL) was added dropwise with a syringe into 500 mL of water with or without stirring at room temperature. [b] Estimated by optical microphotograph or scanning electron micrograph observations. [c] A: Hg lamp at 0°C for 4 h. B: Sunlight at room temperature for 2 days. C: Hg lamp at 30°C for 4 h. D: Hg lamp at room temperature for 24 h. After polymerization, the unreacted monomer was extracted with chloroform at room temperature. [d] In trifluoroacetic acid at 30°C. [e] $M_w = 7.62 \times 10^4$, $M_w/M_n = 2.00$ by GPC. [f] $M_w = 7.01 \times 10^4$, $M_w/M_n = 2.23$ by GPC. [g] $M_w = 8.64 \times 10^4$, $M_w/M_n = 2.37$ by GPC.

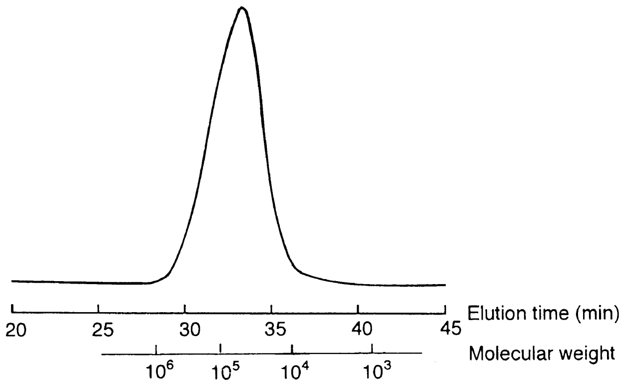

Figure 1. GPC elution chromatogram for poly(EMU) (run 6). Measurement conditions: Eluent, hexafluoro-2-propanol in the presence of sodium trifluoroacetate; Columns, TSG-gel GHH$_{HR}$-H (7.8 mm i.d. × 30 cm) × 2; temperature, 40°C; detector, RI; flow rate, 0.4 mL min^{-1}; sample concentration, 1.0 mg mL^{-1}, sample size, 100 μL, calibration, standard poly(methyl methacrylate)s ($M_w = 2.05 \times 10^3$—1.50×10^6).

stirring. The polymerization was carried out under UV irradiation with an Hg lamp at room temperature for 24 h, because the polymerization rate decreased depending on the size of the crystals used. This crystal size-dependent polymerization reactivity is interpreted by the following polymerization mechanism, which has already been reported,[16] *i.e.*, the polymerization starts by radical formation on photoirradiation and the propagation proceeds at a greater rate by a chain mechanism until the active site reaches the edge or a defect in the crystal. Using the precipitation method for the monomer crystal preparation, the resulting polymers have been revealed to be of $[\eta]$ less than 10^2 cm^3 g^{-1} (runs 6—8). These polymers were characterized by GPC with hexafluoro-2-propanol as an eluent, calibrated with standard poly(methyl methacrylate)s. Figure 1 shows the GPC chromatogram of the polymer obtained in run 6. The elution peak was unimodal, and M_w and M_w/M_n were determined to be 7.6×10^4 and 2.0, respectively. The polymers produced in runs 7 and 8 provided similar results, as shown in Table I. The reason for the molecular weights estimated by the GPC method being smaller than those expected from the crystal size is being examined at the present time.

In conclusion, we have demonstrated that the size of the EMU crystals depends on the method used for the preparation of the crystals and that, as the crystal size decreased, the molecular weight of the polymer decreased as did the polymerization rate. Precipitation was the best method for the preparation of the microcrystals, polymerization of which provides poly(EMU) with a controlled molecular weight. The GPC analysis has revealed that the polymers derived from the EMU crystals prepared by precipitation have an M_w of 7—9×10^4 and a relatively narrow molecular weight distribution ($M_w/M_n = 2.0$—2.4). Further precise control of the molecular weights of the polymer over a wide range and of their molecular weight distribution is now under investigation.

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