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Tacticity control by conformational isomerization in free radical polymerization of acrylate

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ABSTRACT

Contribution of conformational isomerization to polymer tacticity has been studied in free radical polymerization of (−)-menthyl 2-acetamidoacrylate with azo initiators. It has been demonstrated that the chain end of the growing polymer radical, which is generated from the s-*trans* and s-*cis* conformers of monomer, produces stereoselectively new *R* and *S* configurational quaternary carbons, respectively, for the attack of monomer. In addition, polymerization reactivity of both conformers is indistinguishable under the present conditions, and the polymerization is considered to proceed through a chain-end controlled mechanism, which excludes a penultimate unit effect on tacticity in the polymerization. The results obtained would give a clue to understand an origin of tacticity in conventional free radical polymerization of acrylates.

1. Introduction

The majority of research in radical polymerization has focused on the stereoregulation of polymer and polymerization [1,2]. Control of tacticity, in particular, has extensively been interested and the polymerization of olefins bearing bulky substituents or the polymerization in the presence of coordination reagents, polymer matrices, and inclusion compounds has been studied to obtain a high isotactic or syndiotactic polymer [3]. Lewis acids [4,5] and solvents like alcohols [6], for instance, form a complex with radical and/or monomer to change the bulkiness and spin density [7] of the substrates and sometimes enhance the isotacticity of the resulting polymer, e.g., isotacticity from 7 to 63% for the polymerization of *N*-methyl methacrylamide by the addition of $Yb(OTf)_3$ [8]. In replica polymerization of methyl methacrylate, syndiospecific [9] and isospecific [10] propagations have taken place in the presence of the isotactic and syndiotactic polymer matrices, respectively. High isotacticity of polymer has also been performed using bulky olefins substituted by aryl group in the ester moiety, e.g., achiral arylmethyl methacrylates [11], *N*-arylmethyl methacrylamides [12], and diphenyl acrylamides [13]. The origin of these stereospecific radical polymerizations, however, has little been revealed yet, and the mechanism of the polymerizations has only abstractly been concluded to some steric hindrance or a complexation between substrates without any further precise argument.

Several groups have been employed chiral auxiliary to control the stereochemistry in radical additions of small molecules including α,β-unsaturated amides [14–16], Oppolzer's camphor sultam [17], fumarates [18], and they have discussed on the mechanism of the stereospecificity. Porter and his coworkers have studied the control of the stereochemistry of radical additions, e.g., dimerization and trimerization, of chiral acrylamide, and found that pyrrolidine acrylamide would give two stereoisomers with *S* and *R* configurations for the attack of α-amide radical in large excess of one isomer to the other [14,15]. High selectivity similar to the pyrrolidine has also been observed in the radical reactions of chiral oxazolidine acrylamide [16]. Interestingly, the oxazolidine can polymerize to give a polymer with isotacticity as high as 92% [16]. The mechanism giving preferentially isotactic sequence is believed to be the result of one-sided facial selectivity in the addition of the monomer to the same growing radical face caused by the chiral auxiliary. Presence of chiral center in acrylamide derivatives, however, does not always lead to an isotactic polymer. Radical polymerization of chiral acrylamidosulfonic acids, for instance, has been known to give essentially an atactic polymer [19]. As is well known, an amide has a rigid structure, i.e., the rotation around carbon–nitrogen bond is restricted by the conjugation of π electron of C═O group with a lone pair on nitrogen atom [15]. Thus, most of the stereospecific chiral auxiliary radical polymerizations have concerned to an amide monomer. Unfortunately, however, the mechanism giving such an isotactic or atactic polymer has not been revealed yet even for an amide polymerization.

We report herein how tacticity can arise in free radical polymerization of acrylates, e.g., why the probability of *meso*- or *racemo*-propagation, P_m or P_r, cannot become 0.5 in most of the

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radical polymerizations, e.g., P_m typically lies in the range 0.4–0.5 for vinyl monomers and 0.2–0.5 for 1,1-disubstituted monomers [20]. It has been reported for acrylate (**1**) used in this study that an isotacticity of polymer increases with increasing conversion (tacticity mutating polymerization), i.e., decreasing monomer concentration even in conventional conditions at moderate temperature, and in the polymerization near ceiling temperature **1** generates a helical polymer (Scheme 1) [21]. However, **1** can give a random coil atactic polymer at the polymerization temperature far from a ceiling temperature (T_c), e.g., 30 °C ($T_c = 75.4$ °C in [**1**] = 2.0 mol/l in benzene) [22]. Well-known chiral auxiliary radical polymerization of amides and indene [23] is an isospecific polymerization system, and therefore it may be distinguished from a conventional radical polymerization system.

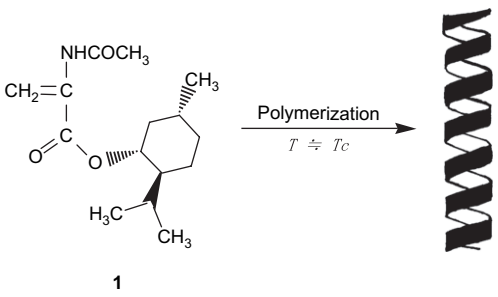
2. Experimental

2.1. Materials

Compound **1** was prepared according to the previous procedure [22], and purified by a column chromatography using a mixture of *n*-hexane and ethylacetate (4:1 wt-ratio) as a developing solvent, $[\alpha]_D = -81.0°$ in $CHCl_3$. ^1H NMR ($CDCl_3$, TMS, ppm) for **1**: 0.76 (d, $J = 7.1$ Hz, 3H, CH_3), 0.90 (d, $J = 7.1$ Hz, 3H, CH_3), 0.92 (d, $J = 6.6$ Hz, 3H, CH_3), 1.0–2.0 (m, 9H, menthyl), 2.13 (s, 3H, $COCH_3$), 4.80 (dt, $J = 4.5$, 11 Hz, 1H, menthyl), 5.85 (s, 1H, CH═), 6.57 (s, 1H, CH═), 7.94 (br s, 1H, NH). Anal. Calcd for $C_{15}H_{25}NO_3$: C, 68.04; H, 9.41; N, 4.87. Found: C, 67.90; H, 9.38; N, 5.02. Commercial grade 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (AMVN), 2,2′-azobis(isobutyronitrile) (AIBN), and 2,2′-azobis(2,4-dimethylvaleronitrile) (ADVN) (Wako Pure Chemicals Co.) were purified by recrystallizations from methanol for AMVN and AIBN and *n*-hexane for ADVN. Deuterated solvent including $CDCl_3$ used for NMR measurement was purchased from Acros Organics Co.

2.2. Measurements

^1H NMR spectrum was recorded on JEOL EX-400 (400 MHz) spectrometer in $CDCl_3$ at 25 °C using tetramethylsilane as an internal standard. ^{13}C NMR spectrum at 100 MHz was measured in 3 wt% D_2O solution at 80 °C with dimethylsulfoxide as an internal standard using JEOL EX-400 spectrometer under conditions of full proton decoupling in 5 mm tube. Typical conditions in ^{13}C NMR spectrum measurements were as follows: sweep width: 20,000 Hz, data point: 32,000, pulse angle: 90°, pulse delay: 2.46 s, and accumulation: 50,000 scans. FT-IR spectrum was recorded in neat or nujol at ambient temperature on JASCO FT/IR-8900 spectrometer. Specific rotation $[\alpha]_D$ at $\lambda = 589.3$ nm (Na–D) was measured on JASCO DIP-360 digital polarimeter in $CHCl_3$ at ambient temperature. Circular dichroism (CD) was recorded on JASCO J-820 spectropolarimeter in ultra-pure *n*-hexane (Wako Pure Chemicals Co.) at 20 °C. Number-average molecular weight (M_n) of polymer was determined by size exclusion chromatography (SEC) using a Tosoh HLC 8020 (Column: TSKgel G7000HHR + G5000HHR + G3000) in tetrahydrofuran at 35 °C on the basis of standard polystyrene. X-Ray diffraction was measured with Rigaku RAXIS-Rapid imaging plate diffractometer using graphic monochromated Cu Kα radiation ($\lambda = 1.54178$ Å) at 23 °C to a maximum 2θ value of 136.1°.



1

Scheme 1. Formation of helical structure in radical polymerization of **1** near ceiling temperature.

2.3. Polymerization

Polymerization was carried out in benzene in a sealed pyrex glass ampoule with shaking at given temperature. The ampoule which contains required amounts of reagents including initiator, solvent, and monomer (2.0 mol/l) was degassed several times by a freeze–thaw method and then sealed under reduced pressure and placed in a constant temperature bath. After the polymerization, the resulting polymer was isolated by pouring the contents of the ampoule into a large amount of methanol. For a photopolymerization, it was performed with ADVN in benzene solution using high pressure mercury lamp (300 W) as a light source in a constant temperature bath at given temperature. The polymers used for the measurements of specific rotation, and CD, NMR, and IR spectra, and SEC were further purified by reprecipitations from the benzene solution into methanol. Finally, the polymer was dried under vacuum at ambient temperature for several days and identified.

2.4. Hydrolysis

Polymer was hydrolyzed with KOH. A solution of KOH (1.0 g) in methanol (30 ml) was added dropwise to benzene solution (20 ml) of polymer (0.2 g) for 1 h at ambient temperature. The precipitated polymer was filtered on a grass filter, and it was further refluxed in KOH (1.0 g) aqueous solution (10 ml) for 2 days. The resultant solution after partial (5.0 ml) removal of water with an evaporator was poured into a large amount of methanol to isolate a hydrolyzed polymer. The reaction proceeded quantitatively, and the polymer furnished for NMR measurement was purified by reprecipitations from the aqueous solution into methanol followed by vacuum drying.

2.5. Hydrogenation

Hydrogenation of **1** was carried out with Pd/C for 48 h under H_2 atmosphere in dry CH_2Cl_2 at ambient temperature. The reaction gave quantitatively a mixture of two isomers of (*R*)-**1a** and (*S*)-**1a**, which were isolated by recrystallization from *n*-hexane, $[\alpha]_D = -72.0°$ for (*R*)-**1a** and $[\alpha]_D = -56.4°$ for (*S*)-**1a** in $CHCl_3$ at ambient temperature. ^1H NMR ($CDCl_3$, TMS, ppm) for (*R*)-**1a**: δ 0.745 (d, $J = 6.8$ Hz, 3H, CH_3), 0.86–0.92 (m, 6H, CH_3), 0.90–1.9 (m, 9H, menthyl), 1.394 (d, $J = 6.8$ Hz, 3H, CH_3), 2.01 (s, 3H, $COCH_3$), 4.70 (dt, $J = 4.2$, 11 Hz, 1H, menthyl), 6.19 (br d, $J = 6.1$ Hz, 1H, NH). IR (nujol, cm^{-1}) for (*R*)-**1a**: 3343 (ν_{NH}), 1720 ($\nu_{C=O}$, ester), 1685 ($\nu_{C=O}$, amide). ^1H NMR ($CDCl_3$, TMS, ppm) for (*S*)-**1a**: δ 0.754 (d, $J = 6.6$ Hz, 3H, CH_3), 0.86–0.92 (m, 6H, CH_3), 0.90–1.9 (m, 9H, menthyl), 1.387 (d, $J = 6.4$ Hz, 3H, CH_3), 2.01 (s, 3H, $COCH_3$), 4.73 (dt, $J = 4.3$, 11 Hz, 1H, menthyl), 6.19 (br d, $J = 6.1$ Hz, 1H, NH). IR (nujol, cm^{-1}) for (*S*)-**1a**: 3343 (ν_{NH}), 1721 ($\nu_{C=O}$, ester), 1652 ($\nu_{C=O}$, amide). Crystals of (*R*)-**1a** and (*S*)-**1a** were produced by relatively first and slow recrystallizations from *n*-hexane, respectively, and stereochemistry was assigned by X-ray crystallography.