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Photodriven Racemization of Optically Active Polymethacrylate Films

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The ability to phototune the optical activity of solid chiral polymers could eventually lead to applications in advanced technology such as optical data recording. In solution, optically active helical polymers,[1] such as poly(cyclohexyldiphenylmethyl methacrylate) (polyCHDPMMA)[2a] and poly(*R*)-1-deuterio-*n*-hexyl isocyanate),[2b,c] can undergo a helix−helix transition (stereomutation) at variable temperatures, resulting in a significant change of optical rotation. The helical polyisocyanate with a temperature-dependent optical activity has been suggested for use as a thermal−optical information storage material.[2c] However, it is more difficult to achieve such a helix transition or optical change in the solid state. Heating optically active solid poly(trityl methacrylate) (polyTrMA) or polyCHDPMMA up to 250 °C leads to polymer degradation, prior to any change in optical rotation.[3] It is generally accepted that the stable, one-handed helical conformation of polyTrMA is maintained by the bulky trityl group. Solvolysis of optically active polyTrMA in methanol affords poly(methacrylic acid) that has no optical activity,[1a] as a result of complete racemization. Conceivably, if removal of the bulky ester group in the solid state can be triggered by light, optically active polymethacrylates should be able to undergo a facile conformational randomization and can, in principle, be used as irreversible optical−optical storage materials. To cleave the acid-labile trityl ester and its analogues, it is highly appropriate to adopt the photoresist chemistry where a triarylsulfonium salt[4] is used as a photoacid precursor. It has been shown that a catalytic amount of the photoacid reacts with poly(*tert*-butyl methacrylate) upon heating, producing poly(methacrylic acid), isobutylene gas, and regenerated acid catalyst.[5] In this paper the first photodriven racemization of optically active films cast from modified polyTrMA and polyCHDPMMA is reported.

High molecular weight optically active polyTrMA and polyCHDPMMA obtained by atropogenic anionic polymerization have low solubility and poor film formability because of their rigid helical structures and high crystallinity. As their oligomers with the repeat units of 20−30 already display large specific rotations,[1d] attaching flexible methacrylate blocks to helical chains would enhance the solubility and improve the film formability. Under appropriate conditions the atropogenic anionic polymerization is living and should allow the production of block copolymers. Thus, living CHDPMMA or TrMA blocks were first synthesized according to the literature procedure[1a,2a] in toluene at −78 °C using the complex of 9-fluorenyllithium and (+)-(2*S*,3*S*)-2,3-dimethoxy-1,4-bis(dimethylamino)butane as an initiator (monomer/initiator = 20/1 for TrMA and 40/1 for CHDPMMA). After most of monomers were consumed (1 h for TrMA and 5−8 h for CHDPMMA), second monomers, methyl methacrylate (MMA), or *n*-butyl methacrylate (BuMA), were introduced into the reaction system. The reaction solution became very viscous rapidly, indicating the progress of block copolymerization. The formation of a block copolymer was confirmed by gel permeation chromatography (GPC). The GPC trace of the CHDPMMA block showed a sharp peak at a longer retention time while a broad peak appeared at a shorter retention time after the addition of second monomer (MMA). Furthermore, a transparent thin film can be cast from the chloroform solution of copolymer **1** but only an opaque film was obtained from the mixture of oligo- or polyCHDPMMA and PMMA. Specific optical rotations of the copolymers synthesized ranged from +198° to +550° at 365 nm, depending on the weight percentage of bulky methacrylates in the polymer chain (Table 1). Increasing the amount of flexible block improves the film formability but decreases the specific rotation, as seen for copolymers **1**, **3**, and **4**. Flexible, tough films could not be cast from copolymers **2** and **5** having a BuMA block and a high helix content, respectively.

To demonstrate the feasibility of the photodriven racemization of optically active polymethacrylates, a small amount (1.0 wt %) of diphenyl-*p*-tolylsulfonium triflate (DPTST)[6] was blended into copolymers **1** and **4**. Transparent films (0.03−0.09 mm thickness) were obtained by casting 10−15% w/w chloroform solutions on circular glass plates (18 mm × 0.2 mm) and drying at 100 °C. Initial optical rotations (α_I) of films were measured at 365 nm and ranged from +0.15° to +0.33° (Table 2). The films were then subjected to irradiation (UV lamp centered at 254 nm) for 2 min. Optical rotations of the irradiated films were taken before and after baking at 120−130 °C for 10 min. No change in optical rotation was detected in samples that were irradiated but not baked or baked but not irradiated, indicating that both irradiation and baking are necessary for racemization.

As for cleavage of poly(*tert*-butyl methacrylate),[5] a catalytic amount of the photoacid is sufficient to split off the acid-labile cyclohexyldiphenylmethyl group from polyCHDPMMA in the solid state. Indeed, optical rotations (+0.16 to +0.33°) of the films cast from copolymer **1** containing 1.0% of DPTST (molar ratio of CHDPMMA/DPTST: 60/1) vanished completely after 2 min exposure to light and 10 min heating. Although physical appearance and UV absorption of the irradiated film showed no visible change, a weak broad band around 3200 cm^{-1} and a weak shoulder peak at 1710 cm^{-1} due to COOH were detected by IR, indicating that the ester cleavage had taken place at some of the CHDPMMA units. After extensive photolysis and thermolysis (3% of DPTST, 5 min irradiation and 10 min baking at 130 °C), the poly(CHDPMMA−MMA) film displayed strong peaks due to COOH. The catalytic nature of the ester cleavage is evidenced by isolation of diphenylmethylenecyclohexane, as expected, from deprotonation of the cyclohexyldiphenylmethyl

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(1) For leading reviews on optically active helical polymers, see: (a) Okamoto, Y.; Nakano, T. *Chem. Rev.* **1994**, *94*, 349. (b) Okamoto, Y.; Yashima, E. *Prog. Polym. Sci.* **1990**. *15*, 263. For representative studies on helix transition and polymerization mechanism, see: (c) Yu, B.; Ding, M.; Wang, Y.; Wang, F. *J. Polym. Sci., Part A*: *Polym. Chem.* **1993**, *31*, 2681. (d) Nakano, T.; Okamoto, Y.; Hatada, K. *J. Am. Chem. Soc.* **1992**, *114*, 1318.

(2) (a) Okamoto, Y.; Nakano, T.; Fukuoka, T.; Hatada, K. *Polym. Bull.* **1991**, *26*, 259. (b) Green, M. K.; Andreola, C.; Muñoz, B.; Reidy, M. P.; Zero, K. J. *Am. Chem. Soc.* **1988**, *110*, 4063. (c) Wilkinson, S. *Chem. Week* **1988** (June 8), 10.

(3) No change in optical rotations was observed prior to thermal decomposition. Thermal stability was studied by differential scanning calorimetry (DSC, heating rate 10 °C/min in nitrogen). A melting point (T_m) of 229 °C was observed in the first scan for polyTrMA, followed by decomposition after melting. The second scan showed no transition up to 250 °C. DSC of polyCHDPMMA displayed a T_m at 220 °C in the first scan and a T_m of diphenylmethylenecyclohexane at 80.0−82.5 °C in the second scan, indicating that thermal decomposition occurred after the first melting.

(4) (a) Crivello, J. V. *Polym. Mater. Sci. Eng.* **1989**, *61*, 62. (b) Dektar, J. L.; Hacker, N. P. *J. Am. Chem. Soc.* **1990**, *112*, 6004.

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(6) Melting point 94.0−96.5 °C (lit.[6a] mp 104−105 °C). This salt, prepared by reaction of diphenyl sulfoxide with toluene in triflic acid and trifluoroacetic anhydride in 45% yield,[6b] generates triflic acid upon photolysis (220−350 nm) in high quantum yield. (a) Miller, R. D.; Renaldo, A. F.; Ito, H. *J. Org. Chem.* **1988**, *53*, 5571. (b) Endo, Y.; Shudo, K.; Okamoto, T. *Chem. Pharm. Bull.* **1981**, *29*, 3753.

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Table 1. Properties of Optically Active Copolymethacrylates

copolymer	composition	wt % of helical block[a]	$[\alpha_1]_{365}$[b]	$[\alpha_2]_{365}$[c]	film
1	CHDPMMA–MMA	46	+610	+198	flexible
2	CHDPMMA–BuMA	58		+290	brittle
3	TrMA–MMA	19	+1300	+236	flexible
4	TrMA–MMA	23		+296	flexible
5	TrMA–MMA	45		+550	brittle

[a] The weight percentage of CHDPMMA or TrMA in feed as well as in the block copolymer, as assumed on the basis of nearly quantitative conversion. [b] Specific rotation (deg cm^2/g) of pure CHDPMMA or TMA block at 22 °C in chloroform. [c] Specific rotation of block copolymer at 22 °C in chloroform.

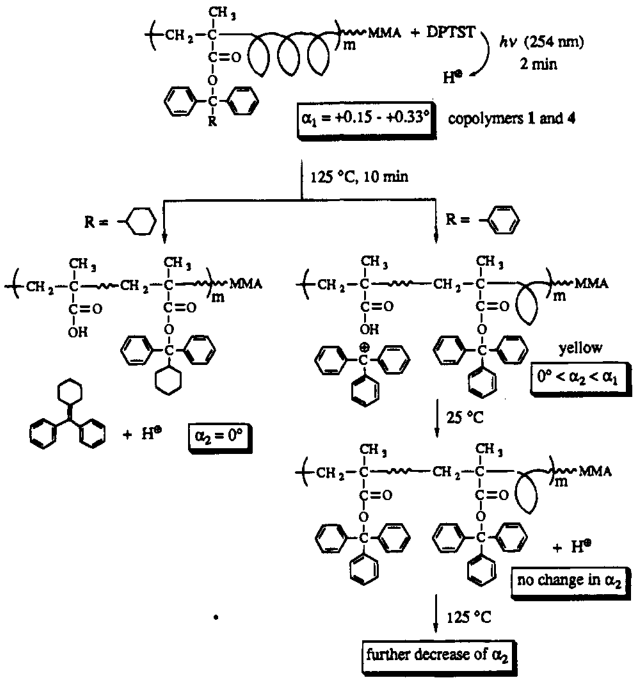
Table 2. Racemization of Optically Active Copolymethacrylate Films

copolymer	composition[a]	thickness (mm)	α_1[b] (365 nm)	α_2[c] (365 nm)
1	CHDPMMA–MMA	0.05	+0.16	0.00
		0.07	+0.26	0.00
		0.09	+0.33	0.00
4	TrMA–MMA	0.03	+0.15	+0.04
		0.05	+0.28	+0.15

[a] Containing 1.0 wt % of DPTST. [b] Initial optical rotation of the film before irradiation. [c] Optical rotation of the film after 2 min irradiation at 254 nm and 10 min baking at 120–130 °C.

cation (Scheme 1).[7] The results have demonstrated that partial loss of the bulky ester groups can result in conformational randomization of helical blocks, which in turn leads to a significant change in optical rotation of optically active solid films. The chemical process initiated by irradiation (writing) involves the photogeneration of an acid, the acid-catalyzed thermal cleavage of the cyclohexyldiphenylmethyl ester, and the formation of the regenerated acid catalyst (Scheme 1). A permanent change in optical rotation (about 0.2–0.3°) of these polymer films is comparable to the Kerr angle (θ_K. typically 0.2–1.0°) of a magneto-optical data recording system[8] and, therefore, should be detectable by similar optical means (reading).

Scheme 1. Photodriven Racemization of Optically Active Copolymethacrylate Films



A stoichiometric amount of the acid is seemingly needed for complete hydrolysis of polyTrMA, since no acidic proton is available from the trityl group. However, the irradiated films of poly(TrMA–MMA) (**4**) containing a catalytic amount of DPTST (1.0 wt %) turned to yellow after baking and showed a moderate decrease in optical rotation (Table 2). UV absorption of this yellow film displayed a new peak at 435 nm, which is attributed to the trityl cation [$(C_6H_5)_3C^+$] produced by photogenerated acid hydrolysis. The formation of the trityl cation was further confirmed by the isolation of trityl alcohol after bleaching the yellow film with water–chloroform. Since the molar ratio of TrMA to the sulfonium salt was about 30/1, only the limited trityl groups could be eliminated from the helical chain during the baking process. Therefore, conformational randomization of a one-handed helical TrMA block took place to a certain extent, and so did the decrease of optical rotation. It was noticed that the yellow color of the treated poly(TrMA–MMA) film gradually faded while its optical activity remained unchanged. Interestingly, the yellow color or the trityl cation resumed when the same film was reheated and the optical rotation further decreased. This suggests that the trityl cation and the carboxyl group in the polymer can recombine back to the ester and the acid is regenerated (Scheme 1). The acid then continues to hydrolyze the other part of the one-handed helical TrMA block during the consecutive baking, which causes a further decrease in optical rotation. The synthesis of processable, highly optically active polymers containing photoresponsive functionalities as reversible optical–optical information storage materials is in progress.

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(7) A white crystalline solid was obtained as the sole product by extracting the irradiated and heated film with hexane: mp 80.0–82.5 °C; ^{1}H NMR (200 MHz, $CDCl_3$) 1.61 (br s, 6 H), 2.25 (br t, 4 H), 7.10–7.30 (m, 10 H); MS (relative intensity) *m/e* 248 ($M^{\bullet+}$, 100), 205 ($M^{\bullet+} - {}^{\bullet}C_3H_7$, 48), 91 ($C_7H_7^+$, 68).

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