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Poly(hemiacetal ester)s: New Class of Polymers with Thermally Dissociative Units in the Main Chain

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Chemical reactions based on “weak covalent bonds” are increasingly being used in the field of polymer chemistry. Homolytic/heterolytic cleavage of such covalent bonds triggered by external stimulation is one of the focal points of current research related to the recent development of stable free-radical polymerization),[1] nonsalt-type latent initiator in cationic polymerization,[2] resist materials,[3] a polymer recycling system,[4] and so on.

The addition reaction of vinyl ether with alcohol or carboxylic acid produces acetal or hemiacetal ester.[5] The hemiacetal ester structure is common in recent polymer chemistry. Higashimura and co-workers succeeded in producing living cationic polymerization with hemiacetal ester in the presence of a mild Lewis acid as the cocatalyst.[6] Thermal properties of hemiacetal esters are also fascinating because they are good candidates for latent initiators in cationic polymerization.[7] Quite recently, our group and Ruckenstein et al. reported polymers with a hemiacetal ester in the side chain prepared by radical polymerization[8] and living anionic polymerization,[9] respectively. The ease of the cleavage of central carbon−oxygen bond in hemiacetal ester structure is attributed to the reduced energy derived from the presence of electron-donating substituent and electron-withdrawing substituent at the ends of the C−O bond, respectively, as in the design of other nonsalt-type latent initiators.[2] As hemiacetal ester structure has such a “weak covalent bond”, it is useful as a building block for the protective group of a functional group, the reactive site, and the initiator in polymer chemistry through appropriate modification. We here report the syntheses and thermal dissociation behavior of new class of polymers, “poly(hemiacetal ester)s” (Scheme 1).

Equimolar amounts of dicarboxylic acids and divinyl ethers in tetrahydrofuran were stirred at room temperature in the presence of 1 mol % of PPTS[10] as acid catalyst.[11,12] At the initial state, the reaction system is heterogeneous because of the poor solubility of dicarboxylic acids. As the reaction proceeds, the reaction mixture became clear and homogeneous in most cases. The obtained polymers had a quite different solubility from the corresponding parent dicarboxylic acids. They are soluble in chloroform, dichloromethane, THF, ethyl acetate, and DMF.

As shown in Table 1, the polymers derived from dicarboxylic acids having alkylene chain (run 1−5) were obtained in 59−89% yield ($M_n = 7.1 \times 10^3$ to 8.5×10^3) except for run 1. In run 1, although the signal assignable to hemiacetal ester structure was observed when the reaction was followed by ^{1}H NMR spectroscopy, no polymer having hemiacetal ester was obtained after the conventional workup. It can be presumed that the polymer derived from oxalic acid decomposed probably due to the low stability. Dicarboxylic acids having other spacers (runs 6−12) afforded the corresponding polymer in 80−99% yield ($M_n = 6.0 \times 10^3$ to 1.4×10^4) except run 10. Even after 24 h, the system did not become clear and homogeneous in runs 9 and 10. This is a marked contrast to other reactions in which high yield polyadditions were accomplished. This is apparently due to the poor solubility of parent dicarboxylic acids, particularly conspicuous in run 10.

The structures of the obtained polymers were confirmed by ^{1}H and ^{13}C NMR and IR spectroscopy. Figure 1 illustrates the ^{1}H NMR spectrum of polymer derived from adipic acid (run 4 in Table 1). Methyl protons (1.40 ppm) and methine proton (5.94 ppm) in hemiacetal ester unit were observed in a 3:1 integral intensity ratio. The $-OCH_2CH_2O-$ protons give two pairs of multiplets in

Scheme 1

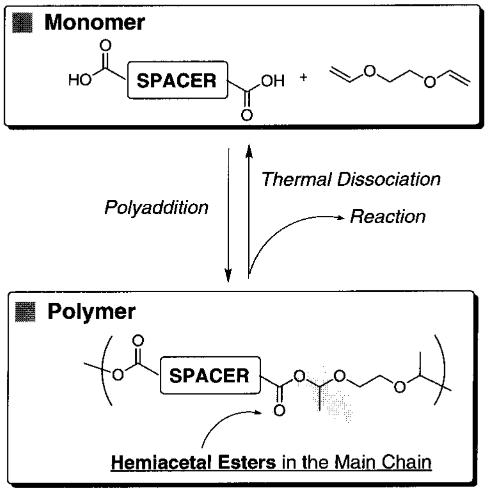
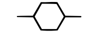
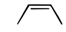
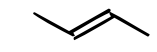
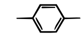
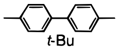
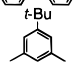
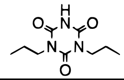


Table 1. Polyaddition of Dicarboxylic Acids (HOOC−R−COOH) with Ethylene Glycol Divinyl Ethers[a]

run	R	yield (%)	Mn[b]	δ (methine)
1	none	0	-	6.06[c]
2	$-(CH_2)_1-$	59	7 100	5.99
3	$-(CH_2)_2-$	74	8 300	5.96
4	$-(CH_2)_4-$	89	8 400	5.94
5	$-(CH_2)_8-$	83	8 500	5.94
6		99	7 900	
7		98	9 300	
8		95	6 000	
9		80	7 300	
10		-[d]	-[d]	
11		98	6 800	
12		98	14 100	

[a] Conditions: dicarboxylic acid, 5 mmol; divinyl ether, 5 mmol; pyridinium *p*-toluenesulfonate, 1 mol%; THF, 2.5 mL; room temperature, 24 h. [b] Estimated by GPC (PSt Stds; eluent, LiBr solution in DMF (5.8 mM)). MWD = 1.5−3.0. [c] Before workup. [d] Trace amount of oligomer formed.

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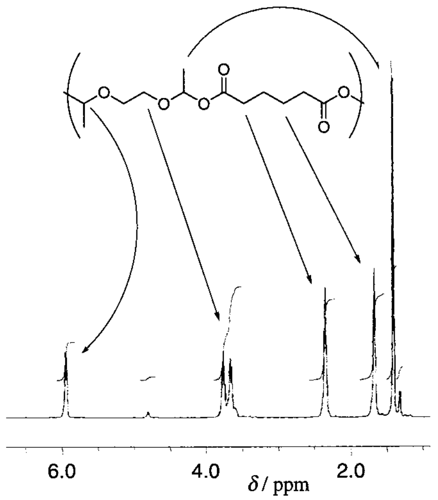

Figure 1. Partial ^{1}H NMR spectrum of polymer derived from adipic acid and ethylene glycol divinyl ether.

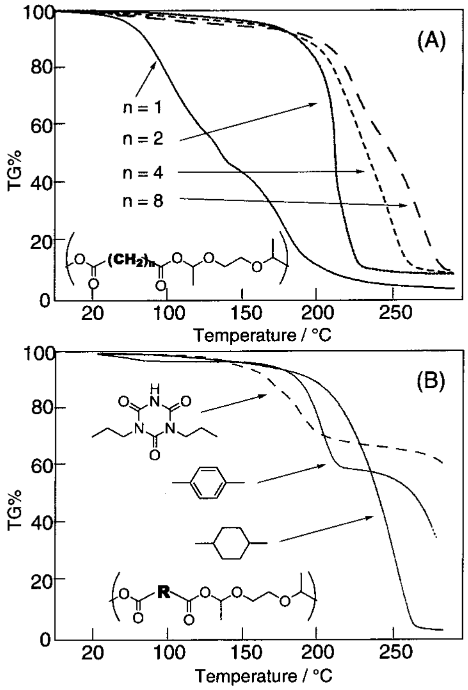

Figure 2. Thermogravimetric analyses of polymers derived from dicarboxylic acids having an alkyl chain (A) and other spacers (B).

a 1:1 ratio, and that can account for the distinctive structure. The protons on the same carbon are regarded as being diastereotopic because of the neighboring chiral carbon. Similar splittings were observed in other all hemiacetal ester structures.[5−9] In IR measurements, the characteristic absorption peak based on carbonyl groups was observed at 1732 cm^{-1}, which is assignable to the hemiacetal ester structures in the polymer backbone. These spectroscopic data clearly revealed that the obtained is “poly(hemiacetal ester)s”.

Thermal properties of the poly(hemiacetal ester)s were evaluated by means of thermogravimetry analyses (TGA). TGA curves of the polymers derived from dicarboxylic acids having alkylene chains ($n = 1, 2, 4, 8$) are shown in Figure 2A. The curves show that the polymers possess significant thermal dissociation abilities and do not show thermal dissociation below 150−200 °C. The dissociation temperature increased by the addition of another methylene group. We have previously reported that hemiacetal ester ($RCOOCHCH_3OR'$) can convert thermally, and that is affected by the electron-attracting ability of the carboxyl group ($RCOO^-$).[7] The dependence of the dissociation temperature upon the spacer length can be due to the inductive effect. Its tendency is also supported from the chemical shift values of methine protons of the polymers because the methine protons in hemiacetal ester unit should shift to lower magnetic field as a result of the inductive effect caused by the ester group on the other side beyond the alkylene chain.

Figure 2B shows the TGA curves of the polymers having hemiacetal esters with variable spacers in the main chain. On the whole, they possess significant thermal dissociation abilities. A similar dissociation temperature was observed in the case of the cyclohexyl derivative in Figure 2B. But, interestingly, the polymer derived from telephthalic acid showed the high dissociation ability (dissociation temperature of 190 °C). This is probably attributed to the mesomeric effect that stabilizes the carboxylate anions. In fact, the polymers derived from fumaric acid and maleic acid also showed a lower dissociation temperature (145 and 190 °C, respectively), although the dissociation temperature of the polymer derived from succinic acid is higher than 200 °C.

The dissociation temperatures of the obtained polymers can be accounted for by both the inductive effect and the mesomeric effect of the spacers in dicarboxylic acids, but there is one exception. One can consider that higher dissociation ability of the polymer containing an isocyanuric acid moiety is due to the increased interaction between the polymer chains. The main interaction might be caused by the hydrogen bonding between the protons of the imide group in isocyanuric acids and the oxygen atoms of the carbonyl group in hemiacetal esters. It seems that hydrogen-bonded hemiacetal ester can easily dissociate because the bonded imide group behaved as electron-withdrawing group for the carbonyl group. Similar results are shown in copolymers derived from vinyl monomer having hemiacetal ester structure.[13] The dissociation temperature was lowered by copolymerization with hydrogen-bonding donating monomer such as acrylamide.[13]

Judging from these results, the dissociation temperature of poly(hemiacetal ester)s may strongly depend on the spacers in parent dicarboxylic acids from the viewpoint not only of the intramolecular effect (inductive effect, pK_a values, and mesomeric effect) but also of their intermolecular one (polarity, hydrogen-bonding ability, and so on).

In summary, the present paper can demonstrate the synthesis of poly(hemiacetal ester)s with various spacers. The use of PPTS as an acid catalyst for the quantitative addition reaction of carboxylic acid with vinyl ether was the breakthrough toward the application to the polyaddition reaction. The dissociation temperature of the polymers can be controlled by a simple molecular design of the spacers in dicarboxylic acid derivatives.

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(11) No ring-opening polymerization of THF was confirmed.

(12) General procedure: dicarboxylic acid (5.0 mmol) and ethylene glycol divinyl ether (5.0 mmol) in dry tetrahydrofuran (2.5 mL) were stirred at room temperature in the presence of 1 mol % of PPTS. After 24 h, the reaction mixture was treated with solid base and purified by high-pressure liquid chromatography if necessary.

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