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Synthesis and Characterization of Thermally Degradable Polymer Networks

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Diacrylate and dimethacrylate monomers containing thermally cleavable tertiary ester linkages with different spacer lengths were synthesized and studied. The photopolymerization rates of diacrylates were much higher than those of dimethacrylates. Glass transition temperatures of the prepared networks increased from 55 to 180 °C with decreasing spacer length for diacrylate networks and from 135 to 185 °C for dimethacrylate networks. Isothermal thermogravimetric analyses revealed that the networks were thermally stable up to 150 °C and decomposed smoothly between 180 and 200 °C to form partially dehydrated linear poly(acrylic acid) or poly(methacrylic acid). It was observed that decomposition reactions were dominated by an autoacceleration mechanism. The rate of weight loss was dependent on temperature and spacer length. Although the resulting decomposition products were insoluble in dimethylformamide, methanol, and water due to the presence of intermolecular acid anhydride groups, they were completely soluble in dilute sodium hydroxide and ammonium hydroxide solution accompanied by hydrolysis or ammonolysis of the anhydride units.

Introduction

Multifunctional (meth)acrylates have been widely used to form photopolymerizable polymers for many applications including coatings, adhesives, dental restorative materials, information storage systems, and stereolithographic materials.[1−3] Highly cross-linked networks have many desirable properties for these applications including high strength, very low moisture absorption, and rapid curing.

The resulting intractability of such networks is an aspect of their behavior which is sometimes a significant disadvantage. If networks are designed so that the cross-linked structure possesses a weak link that can be disconnected by simple thermal treatment, there are many possible advantages for a variety of short term applications. For instance, this concept can be applied to the mounting of electronic components in the assembly of printed circuit boards or the temporary fixing of optical components such as lenses and prisms. This approach, known as rework, means that defective parts may be easily replaced or components may be held firmly in place during manufacture but may be removed if so desired.

The concept of disconnecting thermoset networks was originally described for epoxy systems.[4−6] Tesoro and Sastri[4,5] reported that networks containing disulfide linkages could be degraded by treatment with reagents to break the disulfide links into thiols. Buchwalter[6] reported that cycloaliphatic diepoxides with cleavable acetal links provided networks which were easily decomposed and dissolved in a variety of acid-containing solvent mixtures. We have recently reported the incorporation of tertiary esters in epoxy compounds and demonstrated that the epoxy thermosets undergo network breakdown upon heating.[7] However, because of the many ester types present in these networks, the mechanism of decomposition was not clear.

In this paper, di(meth)acrylate monomers containing tertiary ester linkages with different methylene spacer lengths between these groups were synthesized as model materials for the study of thermal network cleavage. Our molecular design was based on the fact that a tertiary ester is subject to breakdown into carboxylic acid and alkene by simple thermal treatment at temperatures lower than primary esters. This straightforward molecular design enables the well-controlled and selective decomposition of networks, and it can be applied to more complex multifunctional (meth)acrylate systems. Photopolymerization behavior and the thermal decomposition properties of the resulting networks were investigated. Solubility of the decomposed product was examined to ensure that these networks had in fact fully decomposed.

Experimental Section

Synthesis of Tertiary Diol. 2,5-Dimethyl-2,5-hexanediol was purchased from Aldrich and was used without further

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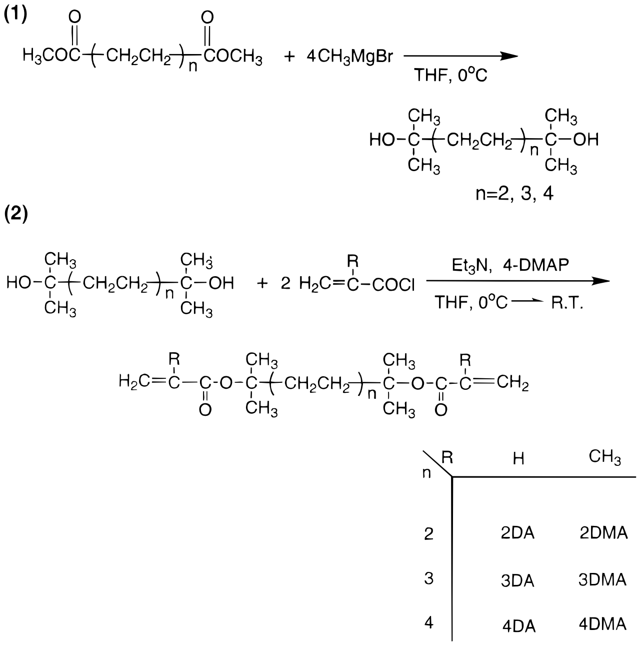
Scheme 1. Preparation of Difunctional Monomers



n \ R	H	CH3
2	2DA	2DMA
3	3DA	3DMA
4	4DA	4DMA

purification. As shown in Scheme 1, the other diols ($n = 2$, 3, and 4) were prepared by the reaction of α,ω-dimethyl carboxylates with methylmagnesium bromide. A typical example is given below for the synthesis of 2,7-dimethyl-2,7-octanediol. To a 500-mL three-necked round-bottom flask fitted with nitrogen inlet, magnetic stirrer, dropping funnel, and a condenser were added 200 mL of dry tetrahydrofuran (THF) and 17.4 g (0.1 mol) of dimethyl adipate (Aldrich) under nitrogen atmosphere. The solution was then cooled to 0 °C using an ice bath. A 133 mL volume of methylmagnesium bromide solution (Aldrich, 3 M in ether, 0.4 mol) was added dropwise over 1 h. After the addition was complete, the reaction vessel was allowed to warm to room temperature, and stirring was continued for an additional 2 h. The reaction mixture was poured onto 350 g of crushed ice and 27 g of ammonium chloride. The upper ether layer was separated, and the aqueous layer was extracted with two 50 mL portions of ether. The combined ethereal solution was washed with dilute aqueous sodium bicarbonate and then was dried with anhydrous magnesium sulfate. After solvent evaporation, the product was crystallized from hexane/acetone (90/10). White crystalline product was obtained (15.0 g, yield; 86%). ^{1}H NMR ($CDCl_3$), δ from TMS: 1.19 [s, 12H, $-C(CH_3)_2OH$], 1.36 [m, 4H, $-CH_2CH_2C(CH_3)_2OH$], 1.43 [m, 4H, $-CH_2CH_2C(CH_3)_2OH$], 1.52 [s, br, 2H, $-OH$]. IR (KBr): 3372 cm^{-1} (O$-$H, stretch); 2971, 2938, 2862 cm^{-1} (C$-$H stretch); 1210, 1148 cm^{-1} (C$-$O$-$C stretch). Mp: 87 °C.

Synthesis of Di(meth)acrylate. Diacrylate (DA) and dimethacrylate (DMA) monomers were synthesized by the reaction of acryloyl or methacryloyl chloride with the corresponding tertiary diols (Scheme 1). Synthesis of 2,7-dimethyl-2,7-octanediol diacrylate (2DA) was as follows.

To a 300-mL three-necked flask equipped with a nitrogen inlet, magnetic stirrer, and a dropping funnel, 8.7 g (0.05 mol) of 2,7-dimethyl-2,7-octanediol, 16.7 mL (0.12 mol) of triethylamine (Fisher), 1.46 g (0.012 mol) of 4-(dimethylamino)pyridine (Aldrich), and 80 mL of dry THF were added under nitrogen atmosphere, and the solution was cooled to 0 °C. The mixture of 10.8 g (0.12 mol) of distilled acryloyl chloride (Aldrich) and 20 mL of dry THF was added dropwise. After 2 h of stirring, the reaction vessel was allowed to warm to room temperature and stirring was continued overnight. Precipitated salts were removed by filtration. A 150 mL volume of diethyl ether was added to the filtrate, and the resulting precipitate was also removed by filtration. The reaction mixture was washed with distilled water and dilute aqueous sodium bicarbonate and was dried with anhydrous magnesium sulfate. Evaporation of the solvents gave an oily residue, which was then purified by column chromatography (silica gel/hexanes). A colorless oily liquid was obtained, yield 3.2 g (23%). ^{1}H NMR ($CDCl_3$), δ from TMS: 1.29 [m, 4H, $-CH_2CH_2C(CH_3)_2O-$], 1.42 [s, 12H, $-C(CH_3)_2O-$], 1.74 [m, 4H, $-CH_2CH_2C(CH_3)_2O-$], 5.66, 6.25 [m, 4H, $CH_2{=}CH-$], 5.98 [m, 2H, $CH_2{=}CH-$]. IR (film): 2978, 2943, 2868 cm^{-1} (C$-$H stretch); 1722 cm^{-1} (C$=$O stretch); 1636, 1620 cm^{-1} (C$=$C stretch); 1299, 1205 cm^{-1} (C$-$O$-$C stretch); 985 cm^{-1} ($=$CH wag); 964 cm^{-1} ($=CH_2$ wag); 812 cm^{-1} ($=CH_2$ twist).

Photopolymerization. 2-Methyl-4′-(methylthio)-2-morpholinopropiophenone (Aldrich), used as a photoinitiator, was added to the liquid monomer (1 wt %). A drop of monomer on a glass slide was squeezed between a cover glass to form a thin monomer film. Photopolymerizations were conducted by exposing films to UV light generated from a UVEXS model 15609 (123 mW/cm^2) from the cover glass side. The distance between the light source probe and the monomer film was 5 cm. Double bond conversions were monitored by FT-IR (Mattson 2020 Galaxy series FT-IR spectrometer).

Dynamic Mechanical Analysis. Dynamic mechanical analyses were carried out with a Perkin-Elmer dynamic mechanical analyzer DMA 7 series for the cured strip samples which are prepared in a DSC pan by a conventional radical polymerization with AIBN in order to determine glass transition temperature. Spectra were recorded at a frequency of 1 Hz. Temperature scans were carried out in air at a heating rate of 2 K min^{-1}.

Thermal Decomposition. Thermal decomposition behavior was investigated with a DuPont 951 thermogravimetric analyzer (TGA) under nitrogen flow. Samples for TGA were prepared by photopolymerization using a 0.5 mm Teflon spacer. After thermal decomposition, the solubility of the residual product was assessed to determine if the networks are fully decomposed using *N*,*N*-dimethylformamide (DMF), methanol, water, 1 N sodium hydroxide solution, and aqueous ammonium hydroxide (28%). Decomposition kinetics was also investigated by in-situ FT-IR analysis. Thin network films were placed on a Mettler hot stage (FP82HT) set at 200 °C, which was mounted into the FT-IR spectrometer. A spectrum was recorded every 5 min. The volatile components, evolved from one network (1DA) film during thermal decomposition conducted in a 2-mL vial at 200 °C, were characterized by gas chromatography (Hewlett-Packard 5890) and ^{1}H NMR (in $CDCl_3$, Varian XL-200 spectrometer).

Results and Discussion

Photopolymerization. Photopolymerization behavior of synthesized DA and DMA difunctional monomers (see structures, Scheme 1) was investigated using FT-IR spectroscopy. Double-bond conversion was determined from the integrated intensity of the $=CH_2$ twisting vibration signal at 812 cm^{-1} for DA and 816 cm^{-1} for DMA. Integration of the C$-$H stretching signals at 2800$-$3000 cm^{-1} was used as a reference to compensate for differences in film thickness. Figure 1 shows the time$-$conversion curves for 2DA (a) and 2DMA (b). For comparison, the conversion data for conventional 1,6-hexanediol di(meth)acrylate (HDDA and HDDMA), in which the distance between two (meth)acrylate groups is the same as that of 2DA or 2DMA, is also shown in Figure 1. Significantly higher rates of polymerization were observed for diacrylates than for dimethacrylates. This is due to the higher reactivity and the smaller size of the acrylate group and the higher flexibility of acrylate backbone.[8]

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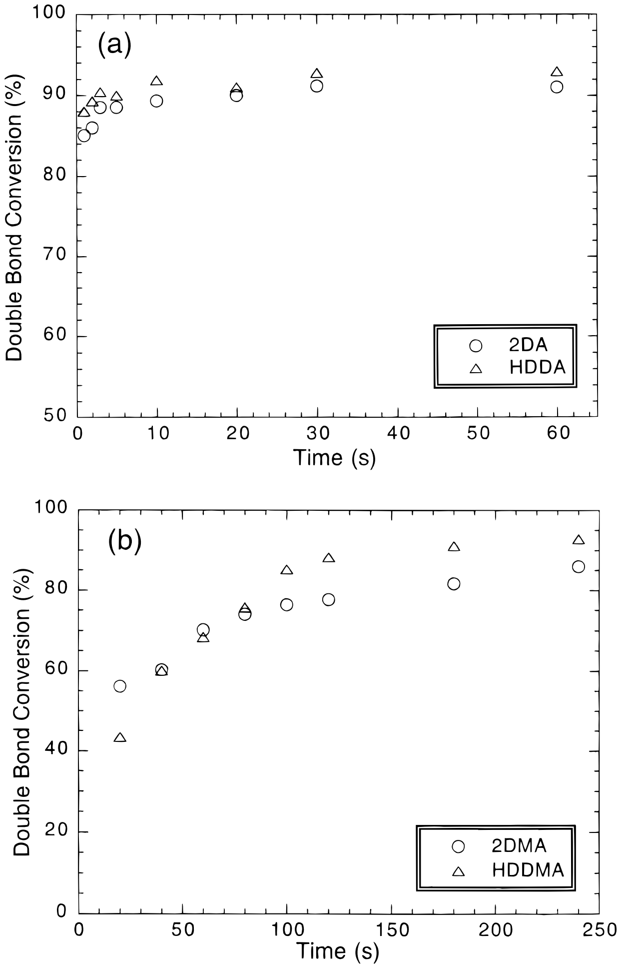

Figure 1. Double-bond conversion measured by FT-IR as a function of the irradiation time: (a) for 2DA and HDDA; (b) for 2DMA and HDDMA.

Table 1. Physical Characteristics of Networks

	double-bond conversion (%)[a]		T_g (°C)	
n	DA	DMA	DA	DMA
1	90	79	180	185
2	91	86	150	165
3	96	85	85	140
4	97	86	55	135
HD[b]	93	93	93	

[a] UV irradiation time was 30 s for DAs and 240s for DMAs. [b] 1,6-Hexanediol diacrylate and dimethacrylate.

Compared with a conventional di(meth)acrylate, conversions of 2DA and 2DMA were slightly lower. It is assumed that the flexibility of backbone and steric accessibility of propagating centers are slightly decreased by introducing methyl groups on the methylene spacer. For both diacrylates and dimethacrylates we examined, similar conversion curves were obtained. As shown in Table 1, a correlation between spacer length and double bond conversion was observed. This may also be attributed to the accessibility of propagating radical site to unreacted pendent double bonds.

Table 1 also lists the glass transition temperatures (T_g) of the networks determined by dynamic mechanical thermal analysis. Although 1DA and 1DMA showed almost the same T_g, the T_g of the other diacrylates was lower than that of its corresponding dimethacrylate. Moreover, the series of diacrylate networks provided a wider range of accessible T_g values compared with those of the dimethacrylates. The differences in T_g between the acrylate and dimethacrylate series could be one cause for differences in the efficiency of double bond conversion. T_g values reported for HDDA networks[9] are also shown in Table 1 and are lower than those of 2DA having the same spacer length. This observation also supports the idea that the added methyl groups also restrict polymer chain mobility.

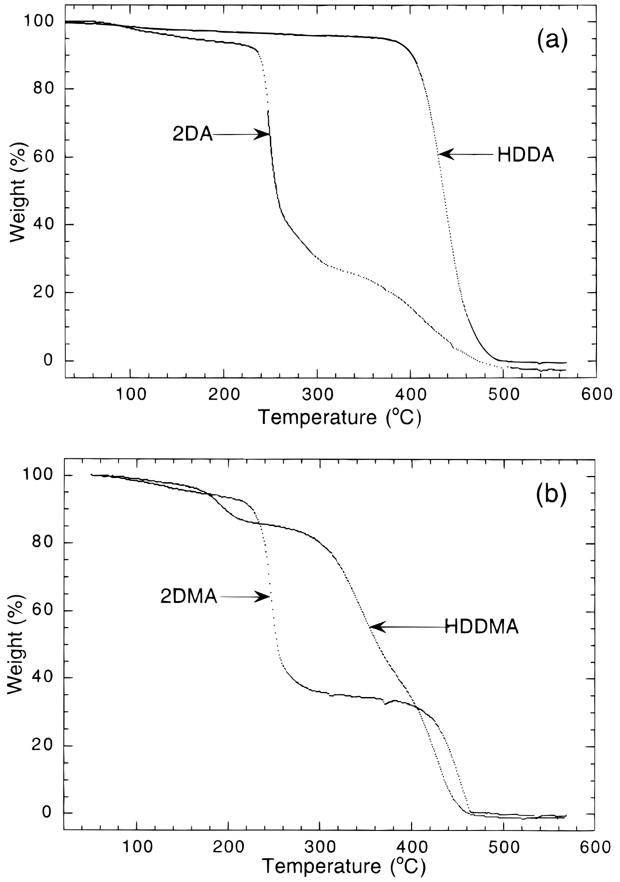

Figure 2. TGA thermograms of networks at 10 °C/min: (a) for 2DA and HDDA; (b) for 2DMA and HDDMA.

Thermal Decomposition. Our main purpose was to design diacrylate and dimethacrylate networks that could undergo thermal disassembly in a specific temperature range and to examine their thermal cleavage chemistry. To study the thermal decomposition kinetics and its mechanism, TGA and IR measurements were conducted. Solubility tests were also carried out to make sure that our decomposed networks were truly soluble.

Figure 2 shows TGA thermograms of networks prepared for this study. For both diacrylates (a) and dimethacrylates (b), a significant difference was observed between the networks containing tertiary esters (2DA and 2DMA) and those containing only primary esters (HDDA and HDDMA). Our networks started to lose weight at ~240 °C followed by a relatively sharp weight loss. This first weight loss was due to the tertiary ester decomposition to form alkenes. At higher temperatures (>350 °C), the polymer backbone decomposed into small molecules. On the other hand, HD-

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(9) Kloosterboer, J. G.; Lijtem, G. F. C. M. *Polymer* **1990**, *31*, 95.

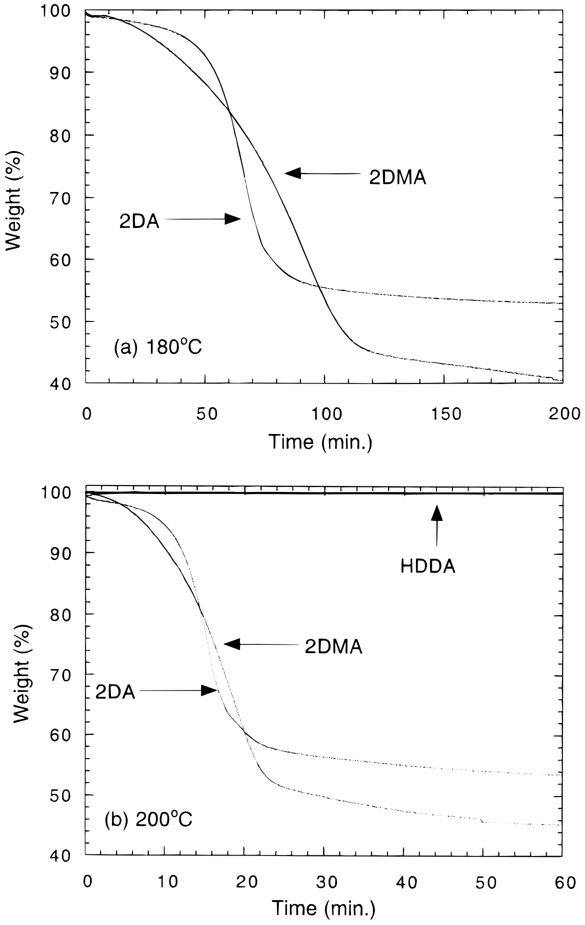

Figure 3. Isothermal TGA profiles of networks: (a) 180 °C; (b) 200 °C.

DMA showed a gradual weight loss over a wide temperature range, because of the decomposition of both ester bonds and the main chain, and to some extent depolymerization. HDDA started to lose weight only at temperatures above ~370 °C.

Although as-cured di(meth)acrylate networks showed no solubility because of their highly cross-linked structure, one might expect that selective ester bond decomposition should lead to solubility changes. After destruction of the cross-linked structure of the networks, the resulting breakdown product should be soluble in commonly used solvents because in our networks each cross-linking point is connected with tertiary ester bonds that will produce a carboxylic acid. Therefore, it was important to investigate the thermal decomposition behavior at a moderate temperature range (<250 °C) to ensure that the tertiary ester bonds of our networks decomposed completely and the resulting polymers became soluble in an appropriate solvent.

Isothermal TGA measurements were carried out at 150, 180, and 200 °C. At 150 °C, no significant weight loss was observed after a 180 min thermal treatment for all networks examined. After heating, networks had almost the same IR spectra as the original ones, indicating that no chemical change occurred at this temperature and that our networks are chemically stable up to 150 °C.

At 180 and 200 °C, our networks decomposed and showed strong temperature dependence. Figure 3 shows the time–temperature dependence curves for 2DA and 2DMA. At both temperatures, weight loss curves of 2DA are characterized by two linear sections, an initial slow rate until ~3% of weight loss followed by an acceleration in rate leading to another linear section. On the other hand, 2DMA did not show a clear linear portion but convex curves during decomposition indicating that the rate of decomposition was gradually accelerated. These kinds of rate acceleration phenomena were also observed in the decomposition of poly(*tert*-butyl methacrylate)[10] and poly(*tert*-butyl acrylate).[11] This is due to an autoacceleration mechanism, where the resulting carboxyl groups catalyze the decomposition reaction of unreacted tertiary ester bonds. As shown in Figure 3b, conventional networks (HDDA) showed no weight loss even at 200 °C.

Table 2. Maximum Decomposition Rates for Networks[a]

	180 °C		200 °C	
n	DA	DMA	DA	DMA
1	1.1 (90)[b]	0.7 (140)	4.0 (21)	3.7 (27)
2	2.1 (65)	1.0 (80)	7.8 (16)	3.9 (18)
3	2.5 (65)	1.2 (85)	9.5 (16)	4.2 (24)
4	1.5 (125)	0.8 (130)	7.0 (20)	3.5 (29)

[a] Maximum rates are based on the TGA data (%/min). [b] The values in parentheses represent the time when the maximum rate was observed.

2DMA showed a larger weight loss than 2DA. This could be explained by the fact that the conversion of 2DMA is lower than that of 2DA and the decomposition of a pendent methacrylate group leads to greater weight loss compared with simple decomposition of a cross-linking bridge. Moreover, depolymerization of the methacrylate networks should also be a reason for the larger weight loss since it leads not only direct weight loss by monomer elimination but also an increased number of pendent methacrylate groups.

The other networks provided almost the same characteristic curves at both temperatures, that is two linear portions for the diacrylates and convex curves for the dimethacrylates. Dimethacrylates always showed larger weight loss than the corresponding diacrylates. The kinetics of decomposition was dependent on spacer length and decomposition temperature. Table 2 summarizes the thermal decomposition rates of networks that were evaluated using rates based on the original weight loss data and the time when maximum rates were obtained. As shown in Table 2, diacrylate networks took less time to reach the maximum weight loss rate compared with dimethacrylate networks at both temperatures. When the number of ethylene units (*n*) was equal to 2 or 3, networks showed the shortest time for both types of networks. When *n* was equal to 1, it is assumed that mobility of the polymer chain is more restricted than in networks with a longer spacer although the concentration of ester groups is higher. In the case of 4DA and 4DMA, the resulting decomposition product alkenes should have higher boiling points. Therefore, the "apparent" rate of decomposition was not as high. A low rate might also be because the concentration of ester groups is relatively lower compared with that of networks having a shorter spacer.

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(10) Grant, D. H.; Grassie, N. *Polymer* **1960**, *1*, 445.
(11) Schaefgen, J. R.; Sarasohm, I. M. *J. Polym. Sci.* **1962**, *58*, 1049.

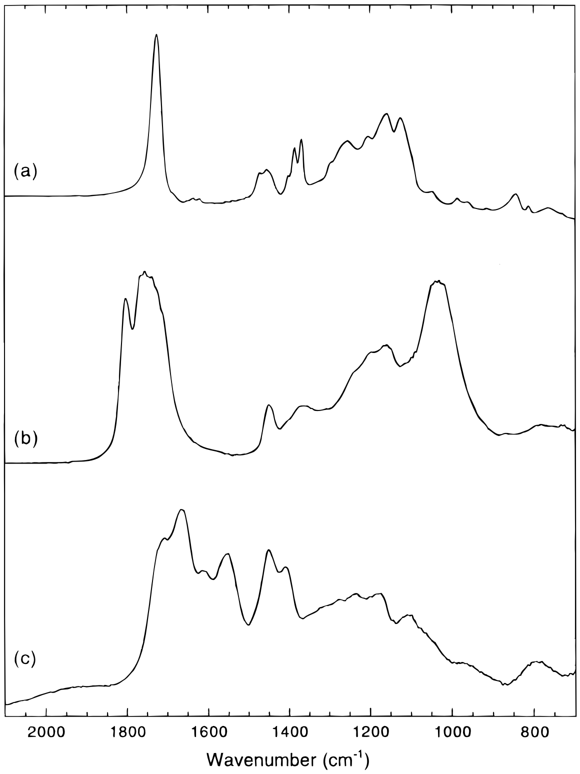

Figure 4. IR spectra of (a) 2DA network and (b) the decomposed product after 60 min at 200 °C and then (c) treated with ammonium hydroxide solution.

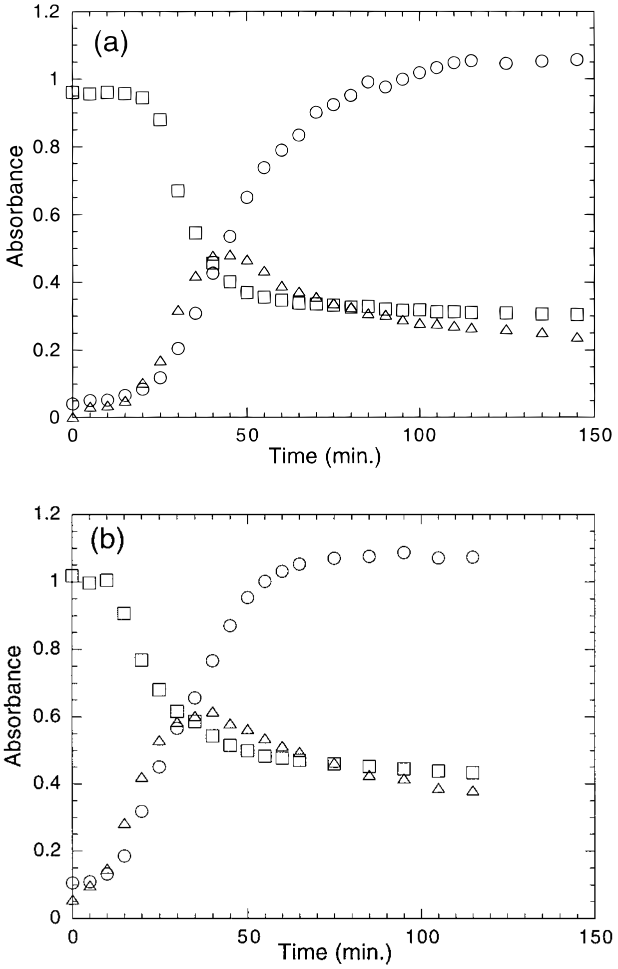

Figure 5. Time dependence of IR signal intensity: (a) 1DA; (b) 2DA. Symbols: (□) $-CH_3$ bending; (▲) −OH stretching; (○) acid anhydride carbonyl stretching.

Scheme 2. Decomposition Reaction of Networks

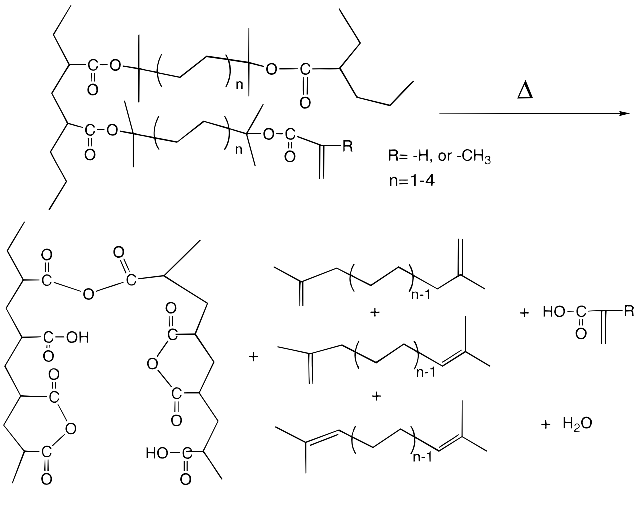

Figure 4 shows the IR spectra of the 2DA network (a) and the decomposition product after treatment at 200 °C for 60 min (b) and when treated with aqueous ammonia (c). In the original network (a), both doublet peaks around 1370−1390 cm^{-1} (which can be assigned to symmetric bending vibration of methyl groups) and a single carbonyl signal near 1740 cm^{-1} were observed. In the decomposition product, doublet signals of the methyl group disappeared, which indicates the complete decomposition of ester bonds. Spectrum b also suggests anhydride formation occurred by elimination of water from the primary acrylic acid units, because of the appearance of peaks around 1030 and 1804 cm^{-1}. In the carbonyl region, many overlapping signals could be observed. This indicates that the resulting product contains unreacted carboxyl groups and various types of acid anhydride groups with both intra- and intermolecular anhydrides.[12]

Decomposition products were insoluble in DMF, methanol, and water, which are the usual solvents for poly(acrylic acid) and poly(methacrylic acid). It is believed that insolubility was associated with the presence of intermolecular anhydride groups. However, this type of cross-linking was expected to be easily cleaved by reagents capable of hydrolysis or ammonolysis of the anhydride units. In fact, decomposition products were readily soluble in sodium hydroxide solution and aqueous ammonia, indicating that our networks did fully decompose and are reworkable. As shown in Figure 4c, anhydride signals (1804 and 1030 cm^{-1}) disappeared after the treatment of ammonia, whereas the carbonyl stretching band of unsubstituted amide (~1680 cm^{-1}) and ammonium salts (~1550 cm^{-1}), the NH_2 deformation band (~1620 cm^{-1}), and the C−N stretching band (~1400 cm^{-1}) appeared.

Figure 5 shows the time-dependent intensity of the IR signal obtained by in-situ measurements. The decrease of CH_3-symmetric vibration band intensity (1370 cm^{-1}) means that tertiary ester bonds break down to form volatile alkenes. A shorter induction time was

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(12) Grant, D. H.; Grassie, N. *Polymer* **1960**, *1*, 125.

observed for 2DA, which is consistent with the TGA results. According to the time dependence of the acid anhydride carbonyl stretching signal intensity (1804 cm^{-1}), it was found that the dehydration reaction started almost simultaneously with the decomposition of ester groups. For both networks, the curves for the −OH stretching band showed a maximum. It is believed that the overall decomposition reactions of our networks proceed predominantly as shown in Scheme 2. The formation of three kinds of alkenes was confirmed with gas chromatography and ^1H NMR by characterization of volatile components from the 1DA network evolved during decomposition.

Conclusion

Diacrylate and dimethacrylate monomers, containing two (meth)acrylate groups connected to tertiary ester bonds, were designed to take advantage of the fact that tertiary esters readily decompose to carboxylic acid and alkenes by simple thermal treatment. The synthesized diacrylate monomers photopolymerized much faster than the corresponding dimethacrylates. Diacrylate networks provided a wide range of glass transition temperatures over the same spacer length range. At moderate temperatures (180 and 200 °C), these networks were shown to decompose smoothly to form partially dehydrated poly(acrylic acid) or poly(methacrylic acid) and volatile alkenes. In the decomposition process, an autoacceleration was observed where the initially formed carboxylic acid groups catalyze subsequent decomposition reactions. Decomposed products were completely soluble in basic solutions, indicating that our networks were fully decomposed and can be removed by a simple thermal treatment followed by washing with a base solution.

Acknowledgment. The authors acknowledge the following people who assisted in polymer synthesis and characterization: Shu Yang and Ron Heddon. For technical consultation, we also thank Dr. Hilmar Körner and Prof. C. Cohen. This research was sponsored in part by the National Science Foundation, The Industry-Cornell University Alliance for Electronic Packaging, and the Semiconductor Research Corp. J.-S.C. also thanks the SRC for a Fellowship. The use of the facilities of the Cornell Center for Materials Research (CCMR) is gratefully acknowledged.

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