Preparation and Properties of Photocurable Unsaturated Oligoester Acrylourethanes

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Synopsis

Syntheses of several photocurable resins and their properties before and after photocuring are investigated. Unsaturated oligoester acrylourethanes (IIIa–IIId) are prepared by addition reaction between four types of hydroxy-terminate unsaturated oligoesters (Ia–Id) and intermediate of adduct II. The former is prepared by addition-condensation reaction of glycols and maleic anhydride, while the latter is prepared from 2,4-TDI and equivalent HEMA by addition reaction in the presence of stannous octoate with THF as solvent. From the decrease of NCOs characteristic absorption peak at 2250 cm^{-1} of IR spectrum, the conversions of the reaction of 2,4-TDI with HEMA and hydroxy-terminated unsaturated oligoesters were calculated. The unsaturated photocurable resins are compared with saturated oligomers (obtained by replacing maleic anhydride with succinic anhydride) with regard to curing rates and mechanical properties. Properties of pure oligomers are determined both before and after hardening. If added with reactive monomers, the oligomers thus cured are found to possess better properties than otherwise. Among the monomers, HEMA proves to be especially helpful in the increase of mechanical properties. Above all, combined use of IIIb oligomer and HEMA serves the best purpose for metal coating.

INTRODUCTION

With the recent demands for low pollution, conservation of resources and reduction of energy consumption in industries, nonsolvent resins have been widely used for coating, painting, adhesion, and insulation in recent years.[1] On the other hand, high-intensive radiation energies[2] such as ultraviolet (UV) light, electron beams, radio frequency, pulse light, and electromagnetic spectra, have been developed to alter the conventional thermal processes, thus enabling photocurable resins[3-6] to enjoy rapid growth and wide acceptance in many industries. Generally speaking, photocurable resins consist primarily of reactive oligomer, mono- or polyfunctional reactive monomers, photoinitiators, and thermal inhibitors. The most commonly used photocurable resins are oligomers with both of their ends possessive of high reactive acrylate or methacrylate monomer units.

There are a great number of articles and patents on photocurable resins such as unsaturated polyester types,[7] epoxy acrylate types,[8-10] acrylate or methacrylate types,[11-14] urethane types,[15-24] among others. However, detailed investigation about unsaturated oligoester acrylourethane of hydroxyethyl methacrylate (HEMA) monomer unit has not been reported. Hence, this paper studied the synthesizing of a series of photocurable resins from unsaturated oligoester in the hope that the unsaturated double bonds within the oligomers can increase crosslinking densities, which in turn will improve the mechanical properties of cured resins.

EXPERIMENTAL

Materials

Reagents and Monomers

Ethylene glycol (EG), 1,4-butanediol (BD), diethylene glycol (DEG), poly(ethylene glycol) (PEG) with $M_n = 300$, maleic anhydride (MA), and succinic anhydride (SA) used in synthesizing unsaturated oligoester were reagent-grade without further purification. 2,4-Tolylene diisocyanate (TDI) and 2-hydroxyethyl methacrylate (HEMA) used in synthesizing unsaturated oligoester acrylourethane, along with reactive monomers, such as N-vinyl pyrrolidone (N-VP), trimethylol propane trimethacrylate (TMPTMA), N,N-dimethylamonoethyl methacrylate (DMAEMA), methyl methacrylate (MMA), and acrylic acid (AA), to be used in preparing photocurable resins were extra pure grade from Tokyo Kasei.

Solvents

THF was distilled before use and acetone was used without further purification, and both were reagent grades.

Syntheses

Synthesis of Unsaturated Oligoester

A four-necked flask was equipped with a magnetic stirrer, condenser, thermometer, and nitrogen inlet. In the flask was placed diol (such as EG, BD, DEG, and PEG) and anhydride (such as MA and SA), with the molar ratio of diol and anhydride at 2.3:1. The mixture was heated at 120°C for 3 h and then at 180–190°C for another 15 h, when water formed from the condensation reaction was observed to distill continuously from the reactor. After the acid number was below 5, the mixture was distilled to remove the unreacted materials under reduced pressure. The yield was about 86% of the reagent of MA. The resulting hydroxy-terminated unsaturated oligoester turned out to be a slightly yellowish transparent viscous liquid.

Synthesizing the Intermediate Adduct of HEMA to 2,4-TDI NCO Para-Position

A four-necked flask was equipped with magnetic stirrer, dropping funnel, condenser, thermometer, and nitrogen inlet. In the flask was placed 69.6 g (0.4 mol) of TDI, 0.24 g (0.2 wt %) stannous octoate as a catalyst and 100-mL anhydrous THF as a solvent; then 52 g (0.4 mol) of HEMA, which was equivalent to the 2,4-TDI, was added dropwise while cooled in a water bath for 2 h. The resultant was the intermediate adduct of HEMA to 2,4-TDI NCO para-position.

Synthesis of Unsaturated Oligoester Acrylourethane

A four-necked flask was equipped with a magnetic stirrer, dropping funnel, condenser, thermometer, and nitrogen inlet. In the flask was placed an

intermediate adduct of HEMA to 2,4-TDI para-position at 121.6 g (0.4 mol) before 48.9 g (0.22 mol) of unsaturated oligoester was added dropwise in the presence of hydroquinone at 60°C. Aliquots were taken out periodically and analyzed to find out unreacted isocyanate by using the IR method. The reaction was cooled, and the THF was removed until the absorption peak of NCO group at 2250 cm^{-1} disappeared completely; this process took about 4 h. The resultant was a slightly yellowish-green transparent viscous. The yield was about 170 g (100%).

MEASUREMENT OF VARIOUS PROPERTIES

IR Spectra

IR spectra of oligomers were obtained on a JASCO Model A-202 spectrophotometer.

Photocuring

Photoinitator benzoin ethyl ether (BEE) (1 wt %) was added to the oligomer and stirred. Then the mixture was cast between two Mylar films and irradiated by a high-pressure mercury lamp (Model USH-500D manufactured by Ushio Electric Co.), at a distance of 30 cm for various lengths of time.

Gel Content

Oligomers after photocuring were extracted by THF at 60°C for 12 h, and residual polymers were dried and weighed. The gel content was calculated in accordance with the following equation:

$$\text{gel content (\%)} = \frac{\text{wt of polymer after extraction}}{\text{wt of original photocured polymer}} \times 100$$

Molecular Weight

Oligomers (0.5 wt %) in THF solution were injected into a Shimadzu Liquid Chromatography Model LC-5A to obtain GPC so as to determine the molecular weight distribution of various oligomers. The columns used were HSG-10 and HSG-20, the flow rate was 1 mL/min, the chart speed was 0.5 cm/min, the pressure was 50 kg/cm^2, and the process was operated on room temperature. The calibration curve was plotted by using monodisperse polystyrene (standard of M_n = 9000, 4000, and 800) as well as hydroquinone (M_n = 110).

IR Method to Determine the Reactivity of Isocyanates

In the flask that was equipped with a magnetic stirrer, stopper, thermometer and nitrogen inlet, were placed 34.8 g (0.2 mol) of 2,4-TDI, 100 mL of anhydrous THF, and 0.122 g (0.2 wt %) of stannous octoate. The mixture was heated to 60°C under stirring. First, 1 mL of reacting mixture was sampled and put into a 0.1 mm NaCl window liquid sealed cell for IR measuring. The measurement was taken by using JASCO Model A-202 spectrophotometer. Then 26 g (0.2 mol) of HEMA was added to flask for four times at an interval

TABLE I
Reactivities of the Hydroxyl Group with Isocyanate Group

Reaction no.	Weight of HEMA added (g)	Weight of Butanediol added (g)	Weight of absorption peak of 2250 cm^{-1} (g)	Weight loss of absorption peak of 2250 cm^{-1} (g)	% of p-NCO reacted (%)	Overall % of NCO reacted (%)
1	0	—	0.1000	0	0	0
2	8.0856	—	0.0968	0.0032	31.07	15.54
3	8.8182	—	0.0895	0.0105	64.96	32.48
4	5.3990	—	0.0811	0.0189	85.71	42.86
5	3.7195	—	0.0767	0.0233	100.00	50.00
6	—	2.7205	0.0621	0.0379	—	65.02
7	—	2.6027	0.0367	0.0633	—	79.39
8	—	2.1275	0.0132	0.0868	—	91.14
9	—	1.6067	0	0.1000	—	100.00

of 60 min. Sample of 1 mL was taken before each addition to take the IR measurement. The reactivity of isocyanate group was calculated by using the weight of the characteristic absorption peak of NCO at 2250 cm^{-1}. The results are shown in Table I. When the absorption peak of 2250 cm^{-1} grew constant, the NCO in a para-position would have reacted at 100% (however, in view of the NCO groups, the reaction was in fact only 50%, for there was ortho NCO group as well).

Second, 9 g (0.1 mol) of 1,4-butane diol was added to the flask for four times for reaction at an interval of 90 min. Then the same process mentioned above was reapplied. The results are shown in Table I. On the basis of the relevant data (weight loss of absorption peak of 2250 cm^{-1} vs. overall % of NCO reacted), a calibration curve was drawn to determine the reactivities of unsaturated oligoester with 2,4-TDI.

Mechanical Properties

The tensile strength and elongation at the break as well as Young's modulus were determined by the ASTM D-638 test method, using Instron Model 1130.

Viscosity

The viscosities of oligomers were measured in 75 wt % of acetone solution of 25°C by using Brookfield Viscometer Model LVF.

Thermal Properties

The glass transition temperature (T_g) was performed on a 943 Thermo-mechanical Analyzer of DuPont Instruments 1090B Analyzer with a load at 5 g at a heating rate of 2°C/min. The sample at a thickness of about 0.3 mm was measured in a range of −30–120°C.

Coating Properties

Hardness. Pencil hardness was determined as a measure of surface hardness according to JIS K 5651.

Flexibility. Flexibility was assessed by the indenter. A 2-mm φ diameter of mandrels was used to fall on the wedge-shaped specimen in order to examine visually the cracking caused.

Impact Resistance. The impact resistance of a paint film was assessed by using DuPont Impact Tester. A rounded block (0.5 in. φ, 500 g wt) was allowed to fall from 500 mm height on the specimen. Visual examination was made for the surface damage.

Extensibility. The resistance of a surface coating to deformation stress was tested by using Erichsen Extensibility Tester. A ball-ended rod (5 mm φ) was pressed into the uncoated side of a painted test panel in 5 mm depth and was visually examined to find out whether there was any surface crack or not.

Adhesion. The adhesive of the coating to the resin was determined by using the cellophane tape cross-cut test (10 lines by 10 lines cut in 1 cm^2) at 25°C.

Chemical Resistance. HCl, NaOH, and NaCl were each diluted to 5% while acetic acid was diluted to 3%. The specimen with an engraved cross was immersed in each solution for 72 h to explore whether stripping around the cross took place.

RESULTS AND DISCUSSION

The Kinetic Reaction of 2,4-TDI with Hydroxyl Compounds of HEMA and Unsaturated Oligoester

2,4-Tolylene diisocyanate (2,4-TDI) has two functional NCO groups with one in ortho (2) and the other in para (4) positions. As a result of the steric effect of methyl group, the reaction rate at 25°C was determined as $k_{para} = 262$ and $k_{ortho} = 25$, respectively.[25] In other words, the NCO group in the para position is far more reactive than that in the ortho position. Therefore, in case the equimolar ratio between HEMA and 2,4-TDI was at 1:1, the reaction was considered to always occur at the para position when catalyst was present. In fact, the experimental results of the reaction of either HEMA or butanediol with 2,4-TDI exactly coincide with the above supposition as shown in Table I. Now, the reaction of 2,4-TDI with HEMA and with unsaturated oligoester was determined by the IR method, and the reacted ratios of para and ortho NCO groups in 2,4-TDI were calculated from the calibration curve of the decrease of NCO characteristic absorption peak at 2250 cm^{-1}. The reaction of the hydroxyl group of HEMA to para-NCO to form urethane was faster at 60°C than the same reaction at the room temperature (22°C). However, the conversion obtained from the calibration curve in a period of 90 min was only 30% at 60°C vs 20% at 22°C in overall NCO groups, or 60 and 40% at 60 and 22°C, respectively, of the p-NCO group alone. On the other hand, if the catalyst was used, the reaction speed was accelerated both at 60 and 22°C. In fact, it was completed in no more than 30 min. This fact implies that the influence of the reaction temperature is brought to minimum in case the catalyst is present.

The reaction of adduct (II) with unsaturated oligoester showed that in the presence of catalyst and at a temperature of 60°C the ortho-NCO would react completely with hydroxy-terminated unsaturated oligoester in a period of 4 h.
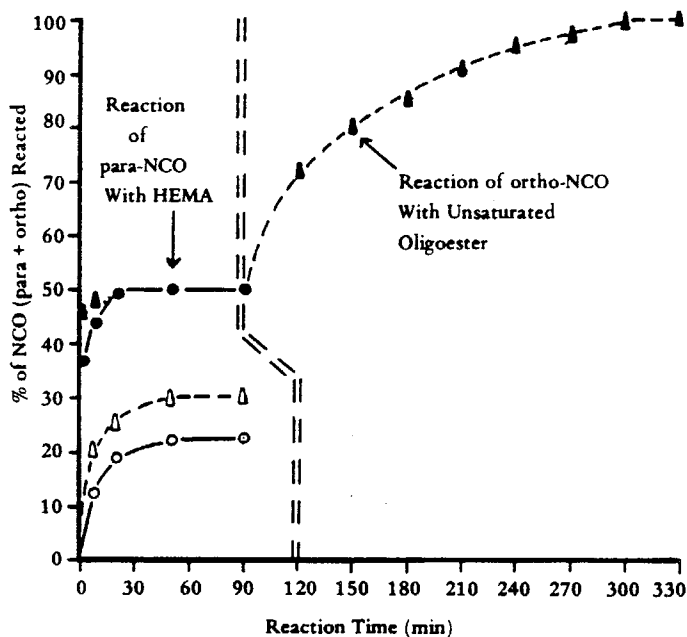
Fig. 1. The conversion of the reaction of HEMA with 2,4-TDI in para position NCO group to form adduct II, and the reaction of adduct II with unsaturated oligoester in ortho position NCO group in various conditions: (O) at room temperature (22°C); (Δ) at 60°C; (●) at 22°C with catalyst; (▲) at 60°C with catalyst.

To avoid the side reaction but to ensure complete reaction, this research was carried out at the room temperature in the presence of catalyst for 90 min in step 1 reaction of para-NCO with HEMA. For step 2 reaction of ortho-NCO with unsaturated oligoester the same catalyst was used at the experiment at 60°C for another 4 h. The results are shown in Figure 1.
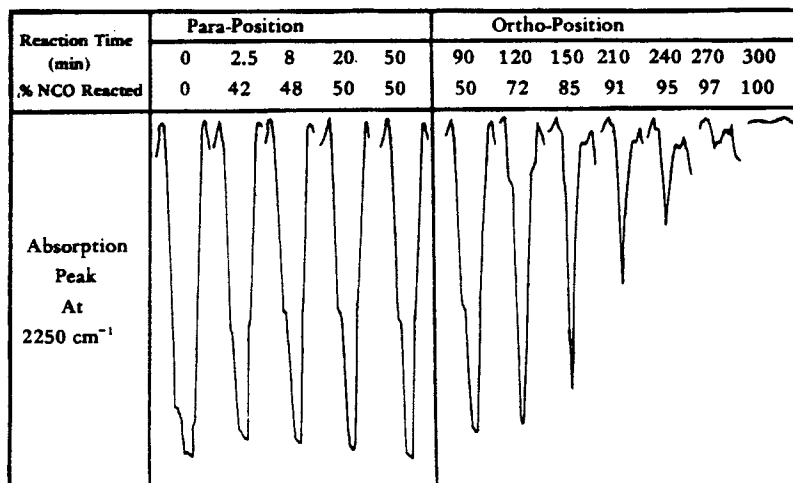
Reaction Time (min)	Para-Position					Ortho-Position						
	0	2.5	8	20.	50	90	120	150	210	240	270	300
% NCO Reacted	0	42	48	50	50	50	72	85	91	95	97	100
Absorption Peak At 2250 cm⁻¹												

Fig. 2. Absorption peak of NCO group gradually decrease with reaction time.

Preparation of Photocurable Resins

Hydroxy-terminated unsaturated oligoesters (Ia–Id) were synthesized from diols (EG, BD, DEG, and PEG) with maleic anhydride. The yield increased with the increase in the reaction temperature and reaction time under the use of catalyst p-toluene sulfonic acid. The degree of polymerization (n) was determined as 1–3 from GPC analysis. The intermediate of HEMA adduct to 2,4-TDI para-NCO [adduct (II)] was reacted with the equimolar ratio in THF solution for 90 min. In the process water bath cooling was used to maintain the reactor in-room temperature so as to counteract the exothermic reaction. Then half-equimolar unsaturated oligoester was added dropwise to adduct (II) with THF in the presence of catalyst stannous octoate under a nitrogen atmosphere at 60°C. Here THF used as a diluent could avoid the gelation. Incidentally, Burlant and Taylor[26] used reactive monomer rather than solvent as a diluent. Whether the yield of unsaturated oligoester acrylourethanes (IIIa–IIId) was complete was confirmed by IR spectrum measurement. The completion was marked by the disappearance of the NCO characteristics absorption peak at 2250 cm^{-1}. Figure 2 shows that the absorption peak of 2250 cm^{-1} gradually decreases with reaction time. The synthetic scheme is shown as follows:
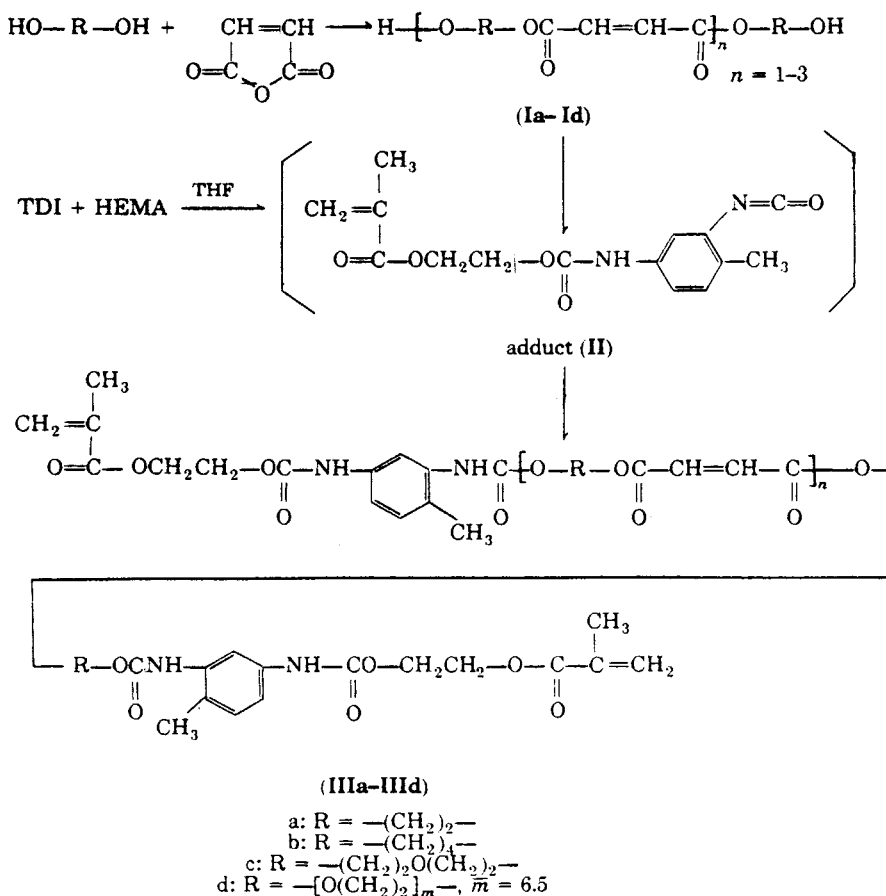
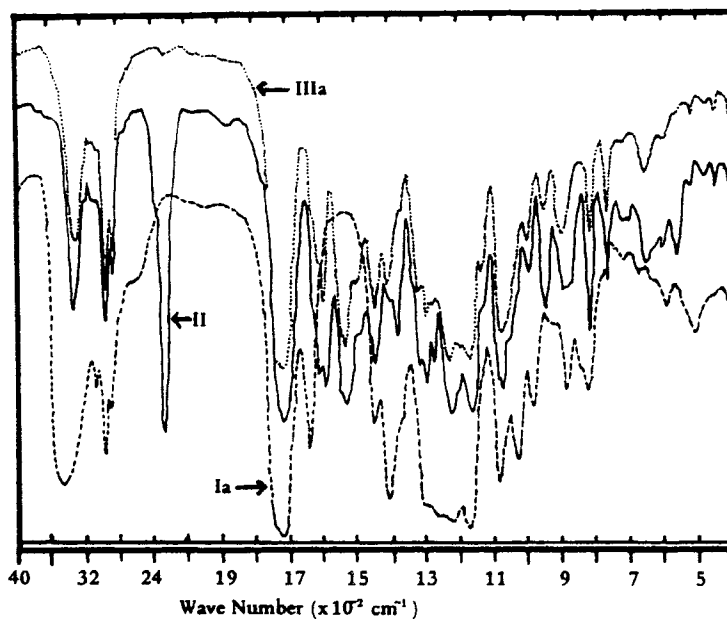The Synthetic Scheme of Unsaturated Oligoester Acrylourethane

Fig. 3. IR spectra of unsaturated oligoester acrylourethane (IIIa), adduct II(II), and unsaturated oligoester (Ia).

IR SPECTRA OF PHOTOCURABLE RESINS

The IR spectra of prepared unsaturated oligoester acrylourethanes such as IIIa and its related oligomers are given in Figure 3, in which unsaturated oligoester (Ia) shows its ester absorption peak at 1710 cm^{-1} and C=C unsaturated group at 1640 cm^{-1}. HEMA that reacted with 2,4-TDI in para-NCO group (adduct II) still retained ortho-NCO absorption peak at 2250 cm^{-1}, while hydroxy group of HEMA at 3450 cm^{-1} was converted to NH absorption peak of urethane of adduct II at 3350 and 1300 cm^{-1}. The absorption peak of NCO in ortho gradually decreased during the reaction of adduct II with unsaturated oligoester. After having reacted for another 4 h, the peak at 2250 cm^{-1} disappeared, indicating that the reaction was completed. The IR characteristic absorption peaks of resulted unsaturated oligoester acrylourethane (IIIa–IIId) showed many functional groups such as urethane NH stretching at 3300 and 1300 cm^{-1}, —COO— at 1720, 1220, 1100, and 1070 cm^{-1}, —CH_2— at 2950 and 2850 cm^{-1}, CH_2= at 3100 and 1450 cm^{-1}, C=C at 1630, 1610, 1410, 990, 940, 890, and 810 cm^{-1}, and phenyl at 1600, 1530, and 760 cm^{-1}.

Fundamental Properties of Photocurable Resins

Other properties, such as molecular weight obtained from GPC, viscosities, refractive index and solubilities are shown in Table II.

Curing Rate of Pure Oligomers as Photocurable Resins

The obtained photocurable resins were cured by UV in the presence of photoinitiator of either benzoin ethyl ether (BEE) or benzophenone (BP). As

TABLE II
Fundamental Properties of Oligoester Acrylourethanes

Properties	IIIa	IIIb	IIIc	IIId	IIIa'[a]	IIIc'[b]
M_n	935	955	1000	1300	800	840
M_w	2460	1660	2100	4340	1240	1230
M_w/M_n	2.63	1.74	2.1	3.34	1.55	1.46
n_D^{25}	1.5286	1.5286	1.5268	1.5165	1.5221	1.5272
Viscosity[c] (cps)	81	148	162	192	70	153
Solubility	(Dissolved in acetone, chloroform, dioxane, THF; insoluble in BTX, alcohols, cyclohexane, and CCl_4)					
Color	(All are transparent yellowish-green)					

[a] Oligoester is synthesized by succinic anhydride with ethylene glycol.
[b] Oligoester is synthesized by succinic anhydride with diethylene glycol.
[c] Viscosity is measured in a viscous of 75% oligomer and 25% acetone.

curing is a radically initiated polymerization, the radical was subject to the influence of the air. In this experiment, when the resin was irradiated in an open state, even if irradiation time was prolonged to 300 s, the surface of the resin remained tacky. For that reason, the curing had to be carried out with the resin sandwiched between two Mylar films. If the covering film was removed immediately after an irradiation of 20 s, the resin surface also remained sticky, and the gel content was lower than 70%. However, if the film was not removed 10 h after the irradiation (this process is defined as post-curing), the surface of cured resin was hard and smooth, and its gel content was
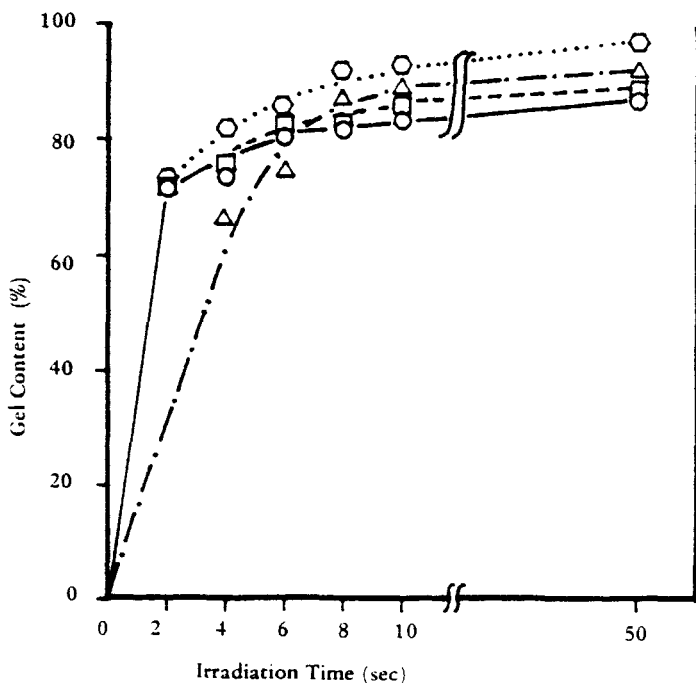

Fig. 4.   The percent of gel content of oligomers at various irradiation times: (○) IIIa; (◯) IIIb; (△) IIIc; (□) IIId.

Irradiation time (s)	2	10	30	40	50
Gel content (%)	73	84	86	87	87
T_g of cured film (°C)	39.5	47	50.5	58	58
Young's Modulus (kg/cm^2)	—	4580	5150	5360	5270
Tensile strength at break (kg/cm^2)	—	190	245	265	230
Elongation at break (%)	—	55	36	30	30

high even if it was irradiated for only 10 s, its gel content could be higher than 85%. There would be no difference whether there was post-curing or not if the irradiation time was prolonged to 40 s. The prepared photocurable resins as mentioned above were found to be better than epoxyacrylate reported[8] in terms of gel content and curing rates.

The curing rates of several kinds of pure oligomers were determined by measuring the percent of gel contents vs irradiation time. The results are shown in Figure 4. All oligomers were cured rapidly in 2 s and they levelled off in about 10 s. Their gel contents ranged from 84 to 95%. Of all the oligomers, IIIb showed the best value in the gel content.

When amine was added to photoinitiator BEE or to BP, the results obtained were incompatible with the results when BEE alone was used.

Effects of Irradiation Time on Properties of Cured Oligomer

Table III shows that mechanical properties, such as tensile strength at break and Young's modulus along with other properties, such as gel contents and T_g of cured oligomer of IIIa, all increase while elongation at break decreases with the duration of irradiation time. The result is shown in Figure 5. These properties become levelled off when irradiation exceeds 40 s. That is because the properties are related to the crosslinking density, and the crosslinking density increases as the irradiation time is extended, which reaches the maximum when the irradiation last 40 s. Beyond that the mobility of the molecular is limited, and therefore the crosslinking density cannot keep on increasing.

That the elongation at break did not appear to be as high as it might be is attributed to the fact that the chain length between crosslinks was not long enough to possess the characteristics of elastomer. In addition, the cured structure was a multirayed star-shaped crosslink[15] possessing low flexibility. Moreover, the testing conditions such as temperature and rate of extension were not in the best.

Properties of Various Cured Oligomers

When the irradiation time of cured oligomers was fixed at 50 s, the oligomers' various properties, such as molecular weight, gel content, T_g, hardness, Young's modules, tensile strength at break, and elongation at break are shown in Table IV and Figure 6. The results show that the molecular
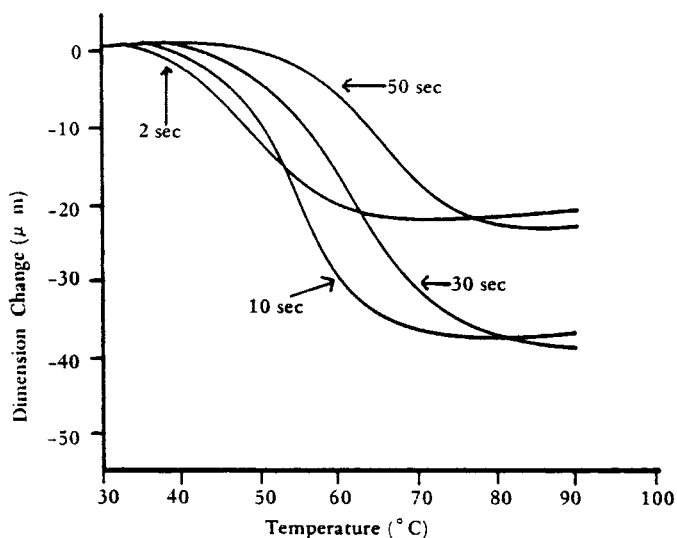
Fig. 5. Glass transition temperature of cured oligomer (IIIa) varied with irradiation times.

TABLE IV

Mechanical and Other Properties of Cured Oligomers Irradiated at a Period of 50 s

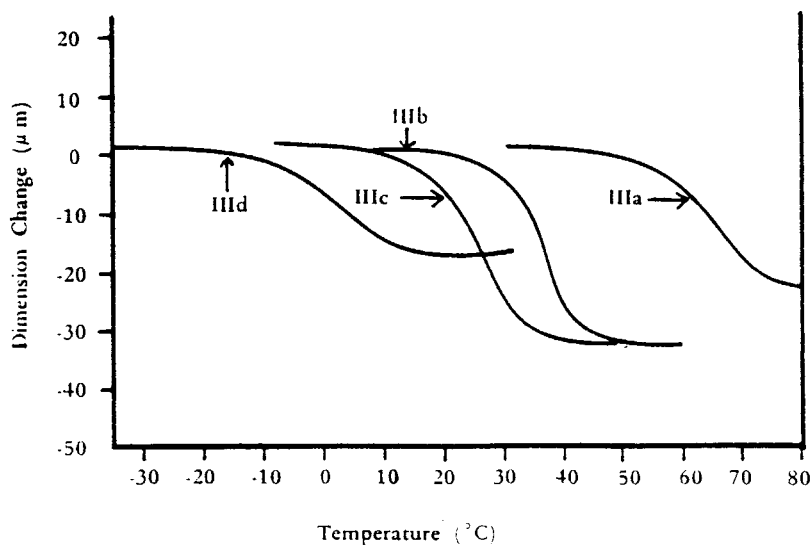| Type of oligomer	IIIa	IIIb	IIIc	IIId	IIIa'	IIIc'
Molecular weight (M_n)	935	955	1000	1300	800	840
Gel content (%)	87	96	92	88	92	89
T_g of Cured Film (°C)	58	34	20	−7.5	35.5	20.5
Hardness (Shore D)	62.5	60	57	38	62	53
Young's modulus (kg/cm^2)	5360	4150	1680	350	4960	1450
Tensile strength at break (kg/cm^2)	265	215	140	130	270	165
Elongation at break (%)	30	35	50	75	35	55

Fig. 6. Glass transition temperature of various oligomers.

weight increases with the decrease of Young's modulus, tensile strength at break, and the glass transition temperature. However, elongation at break increase as molecular weight increases. These results (chain flexibility ascends in the oligomers from IIIa to IIId) coincides with the results of Landel and Fedors's,[27] who maintain that the extension ratio at break is approximately proportional to the square root of the molecular weight of the chain between crosslinks.

The Influence of Unsaturated Double Bonds on the Properties of Oligomers

To examine whether the existing unsaturated double bonds brought about crosslinking, thus increasing the mechanical properties, we substitute succinic anhydride for maleic anhydride to synthesize saturated oligoester acrylourethanes IIIa' and IIIc', which were similar to unsaturated oligoester acrylourethanes IIIa and IIIc, respectively, in terms of molecular structure. The gel contents at various irradiation times show that unsaturated oligoester acrylourethanes were better than those of saturated, especially of IIIc type. In other words, the internal double bonds of oligomers must have participated in crosslinking, thereby increasing the crosslinking density. This result is reflected in Young's modulus. The higher crosslinking density made the chain segment harder than that of the lower crosslinking density of saturated oligomers,
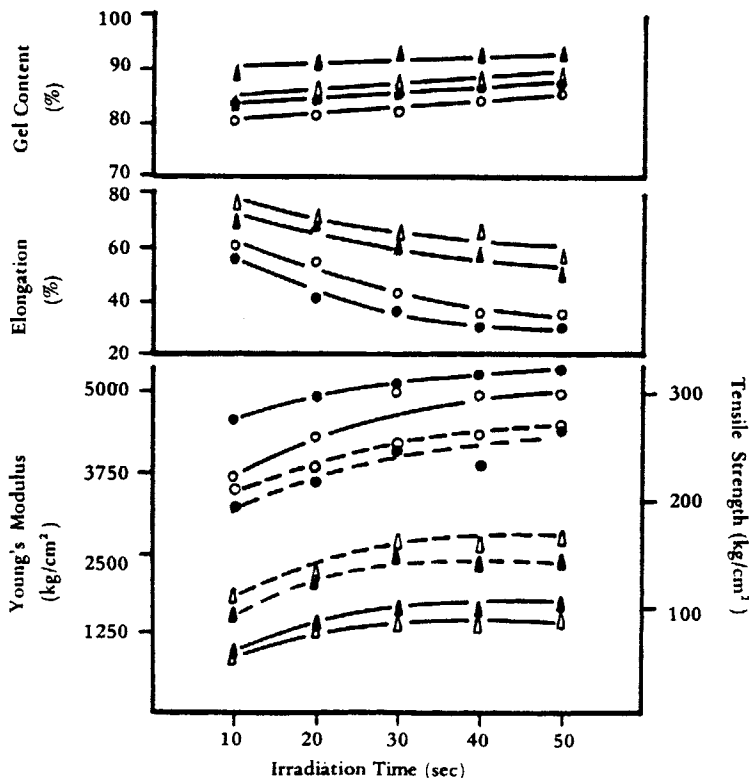

Fig. 7. Comparison of the properties of oligomers with saturated chain segments and oligomers with unsaturated chain segments: (●) IIIa; (○) IIIa'; (▲) IIIc; (△) IIIc'.

TABLE V

Effect of the Reactive Monomer on the Properties of 75% Oligomer Added with 25% Reactive Monomer System[a]

	IIIa				IIIb				IIIc				IIId			
	G%	YM	TS	E	G%	YM	TS	E	G%	YM	TS	E	G%	YM	TS	E
AA	++	++	++	–	±	++	++	–	+	++	++	–	++	++	+	++
MMA	–	++	++	– –	–	++	++	– –	–	++	++	– –	–	++	++	++
HEMA	+	++	+	–	+	±	+	+	±	++	++	+	+	++	+	++
DMAEMA	+	++	++	+	– –	+	+	+	– –	–	–	+	– –	–	–	– –
TMPTMA	+	++	++	– –	+	++	++	– –	±	++	++	– –	+	++	+	– –
VP	+	++	++	–	±	++	++	– –	–	++	++	– –	–	+	+	– –

[a]G% = gel content; YM = Young's modulus; TS = tensile strength at break; E = elongation at break; ±:no change; +:increase; ++:increase remarkable; –:decrease; – –:decrease remarkable.

especially of IIIa type. On the other hand, higher crosslinking density limited the mobility of polymer chains and restricted the double bonds at the chain end reacted; as a result, the breaking strength were not so high as it might be. The cured product showed fragility and inferior quality in comparison with saturated oligomers. The results are shown in Figure 7.

Properties of Oligomer / Reactive Monomer Systems

As mentioned above, pure oligomers had high viscosity and tightly cross-linked structure; therefore, several kinds of reactive monomers were added to reduce viscosity so as to increase flexibility, elongation, and toughness. When oligomer and reactive monomer are mixed together at a ratios of 3:1 in the following reactive monomers, such as AA, MMA, DMAEMA, TMPTMA, and VP, there occurred a remarkable effect on curing rates and mechanical properties. The results are shown in Table V. Of the reactive monomers, HEMA has an increasing effect on gel content, tensile strength, elongation at break, and Young's modulus. The prepared coating of 75% IIIb and 25% HEMA showed the best results for metal coating. The cured coating had the good adhesion (100/100), flexibility, hardness (4H), impact strength, extensibility, and chemical resistances. (For instance, the coating could resist 10% HCl over 120 h, 3% CH_3COOH over 120 h, 10% NaCl over 336 h, and 10% NaOH over 12 h.)

CONCLUSIONS

Several unsaturated and symmetrical saturated oligoester acrylourethanes are synthesized via condensation and addition reactions in THF solution and in the presence of catalyst. The NCO characteristic absorption peak at 2250 cm^{-1} of IR spectrum can be used to determine the conversion of NCO group reacted with the hydroxy group in this study. Properties of synthesized oligomers are compared for the chain segment of saturated and unsaturated, with the results showing that the oligomers of the unsaturated chain are superior in curing rates and mechanical properties. Properties of cured pure oligomers vary with chain structure and molecular weight. Adding 25% of reactive monomer can increase the curing rate and mechanical properties. Of all the systems, the mixture of IIIb oligomer and HEMA is found to be the best for metal coating.

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