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Synthesis of new polyesters with methacrylate pendant groups

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Summary

A catalytic process for synthesis of new polyesters with methacrylate pendant groups is presented. Thus, zinc succinate catalyzed reaction of succinic anhydride with glycidyl methacrylate (GMA) in dimethoxyethane gives linear oligoesters with low molecular weights (1380-2400 Da). The polyester formation takes place via simultaneous ring opening of the cyclic anhydride and oxirane units.

GMA component can be partially replaced with cyclohexeneoxide to obtain polyesters with methacrylate pendant groups in various percentages. Nearly colorless waxy polymers are obtained in excellent yields (69-97 %) within 48-60 h. at 90 ^{o}C. In the study structure of the polymers have been elucidated by conventional spectroscopic techniques and photo-crosslinking of ability of their thin films have been tested by monitoring intensity of methacrylate double bonds, using IR-spectrometry methodology.

Keywords:

Polyester, glycidyl methacrylate, pendant group, succinic anhydride, cyclohexene oxide, zinc succinate, catalyst

Introduction

The growing concern in the radiation curing materials has led to a constant search for polymers and oligomers curable in few seconds. Radical-type photocurable systems are mostly preferred due to their advantages over ionic-initiated systems. Among various photocrosslinkable systems such as polymers with cinnamate [1, 2] or enone functions [3, 4], acrylate containing polymers are of prime importance due to outstanding reactivity of the acrylate double bonds in radical polymerizations [5].

A large variety of telechelics oligomers [6] and multifunctional monomers [7] constituting with acrylate functions are now available on the market. They contain various connecting units, such as ether, ester, carbonate or silicone groups.

Beside those, acrylate functions have been incorporated as pendant groups by reaction of an epoxide containing polymer such as epoxidized polyisoprene, with acrylic or methacrylic acids [8]. Also reaction of phenol-formaldehyde resins with glycidyl methacrylate [9] has been demonstrated to be useful route in preparing polymers with acrylate pendant units. Those approaches involve modification of prepolymers and need tedious processes. Since polymer modification, in generally depends on preparative conditions it is difficult to attain any desired degree of functionality by this method.

In this work we have targeted to more direct way of incorporation of acrylate functions as pendant units. This was achieved by reaction of glycidyl methacrylate with succinic anhydride.

Reaction of epoxy group with cyclic anhydrides gives polyesters by simultaneous ring opening of the reagents [10]. Since water elimination is not needed, this esterification is attractive. However the reaction takes place around 140 ^{o}C without catalyst. Such a process yields colored polyesters owing to partial decomposition of the products. Catalyst is essential to prepare polyesters at lower temperatures [11]. Some zinc complexes [12] have proven to be effective in this reaction. Similar reaction of epoxides with CO_2 (anhydride of carbonic acid) yielding polycarbonates is also complicated. Because many catalysts studied yield polymers with excess of ethyleneoxide segments [13]. As a result the problem seems not to be settled yet.

In the present work we have demonstrated that a simple salt, zinc (II) succinate is useful catalyst for the reaction of succinic anhydride with GMA or cyclohexeneoxide, even it is insoluble in the reaction medium. In the study structure of the polymers have been elucidated by ^{1}H-NMR.

Experimental

Materials:

Commercial *glycidyl methacrylate* (Fluka) contains up to 5 % of glycidol. This must be removed prior to use in the reaction with succinic anhydride. This was carried out as follows: Fifty mL of glycidyl methacrylate was mixed with 100 mL of diethyl ether in a separatory funnel. The resulting solution was washed with 5×100 mL of distilled water (containing 0.01 % hydroquinone). The ethereal layer was dried with anhydrous Na_2SO_4 and filtered. The ether was removed by rotavapor. The yield of glycidol-free product was 38 mL.

Zinc succinate was prepared as follows: Disodium succinate (8.1 g, 0.05 mol) was dissolved in 60 mL of ethanol-water mixture (1/ 1). To this solution, 40 mL ethanol solution of 6.81 g, anhydrous $ZnCl_2$ (0.05 mol) was added while stirring. The precipitate was collected and digested in 10 mL of water. After filtration and washing with alcohol and ether (30 mL of each), it was dried under vacuum at 50 ^{o}C, for 24 h. The yield was 5.7 g (69.8 %), Mp: 148 ^{o}C (lit. 149 ^{o}C).

Cyclohexeneoxide (Aldrich) was purified by distilling under vacuum (58 ^{o}C, at 30 mm).

Dimethoxy ethane (Fluka) was dried over molecular sieves.

Succinic anhydride (Fluka) was used as purchased. All the other chemicals were used as supplied.

Preparation of the Polyesters

The polyesters were prepared by reaction of succinic anhydride with equimolar amounts of epoxy compounds in presence of zinc succinate as catalyst. Glycidyl methacrylate was the main epoxy component. Cyclohexeneoxide was used as secondary epoxy component in order to dilute GMA component.

The procedure was as follows: To a 100 mL volume of two-necked flask equipped with a reflux condenser and a nitrogen inlet, there were added 4 g (0.04 mol) succinic anhydride, 5 mL dimethoxy ethane and a total 0.04 mol of GMA – Cyclohexeneoxide mixture. The flask was mounted in a thermostated oil bath at 90 ^{o}C. Nitrogen was flushed through the mixture and 50 mg (0.27 mmol) Zn ($C_4H_4O_4$), 0.02 mL methyl isobutyl ketone (as inhibitor) was added. The mixture was stirred for 60 h. After cooling the reaction content was poured into 150 mL of 0.1 M HCl solution and precipitated by adding 30 mL of 25 % NaCl solution. The supernatant was decanted and the residue was dissolved in 30 mL ethanol. Then it was reprecipitated in 100 mL of 3 % Na_2CO_3 to remove residual succinic acid. 50 g cracked ice was added to the mixture to facilitate the precipitation. The product was collected by filtering.

The practical yields varied in 69-97 % range for various GMA / CHO ratios.

It is important to note that, the reaction with pure GMA component gave crosslinked polymers, in few cases, even in the presence of hydroquinone or 4-t-butyl phenol as polymerization inhibitors.

Photo-crosslinking of the Polyester Films

One gram of the polyester sample was dissolved in 5 mL of THF and 50 mg benzophenone was added as sensitizer. About 3 / 4 of the solvent was evaporated and thin films (about 0.1 mm) were casted on to glass plate (2×4 cm) from the viscous solution by means of doctor blade. The films were irradiated in a Rayonet Merry-go-Round type photometer equipped with 16 lamps emitting light nominally at $\lambda = 350$ nm and a cooling system. Extent of the photo crosslinking reactions were monitored, after short exposures by diminishing integral ratios of the bands in 1620-1760 cm^{-1} range to those of the bond at 1570 cm^{-1} in their FT-IR spectra.

Techniques

1H-NMR spectra were taken by a Bruker 250 MHz NMR spectrometer, using $CDCl_3$ as solvent.

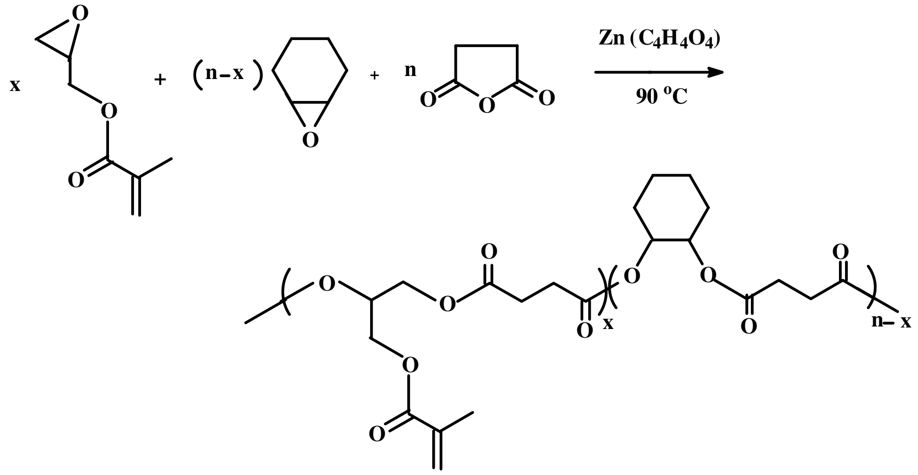
Gel Permeation Chromatograms (GPC) were recorded by an Agillant 1100 series instrument consisting of a pump, a refractive index-detector and Waters Styrogel (HR4, HR3, HR2) columns. THF was used as eluent at a flow rate of 0.3 mL / min.

Infrared spectra were taken by Perkin Elmer One B model FT-IR spectrometer.

Viscosities were determined by capillary viscometer technique using Ubbelohde viscometer.

Results and Discussion

Reaction of glycidyl methacrylate with succinic anhydride provides a simple pathway for preparing polyesters with methacrylate pendant groups (Scheme-1). Since water elimination is avoided, polyester formation by epoxy-cyclic anhydride reaction is of great interest. However, this process is not straightforward and does not proceed without catalyst.



Scheme-1: Polymerization of glycidyl methacrylate with succinic anhydride and cyclohexeneoxide

Indeed the yield was less than 1.5 % for 72 h of the reaction time at 120 °C without catalyst. In some cases crosslinking took place in few hours of the reaction at this temperature.

Herein, we describe simple catalyst; zinc succinate which makes the reaction possible at 90 °C. Although it is not soluble in the reaction mixture, satisfactory yields can be attained for 60 h of reaction times (Table-1).

Table-1: Yields and molecular weight of the oligoesters

Entry	GMA[a] (%)	Yield[b]	M^c_w	M_n
1	0	97.1 %	2600	2400[d]
2	2	92.0 %	1400	1380
3	5	94.7 %	1400	1390
4	10	95.4 %	1450	1410
5	100	69.0 %	1800	1680

a) Mol percentage of GMA b) practical yield c) by GPC d) product of 48 h of reaction time.

The GMA content can be changed by substituting with cyclohexeneoxide as a secondary epoxy component. By this way a series of polyesters with various GMA contents were prepared. GPC experiments revealed that the resulting materials were low molecular weight (Mn = 1680-2400 Da) oligoesters.

1H-NMR spectra of the polymers (Figure1, 2) indicate expected polyester structures. Thus, ethylenic proton signals of GMA component, (Figure1) are observed at 6.1 (cis-H) and 5.6 (trans-H) ppm. Methyl group protons of this component give a singlet at 1.9 ppm. $–CH_2-O$ protons attached to succinate and methacrylate groups give broadened signals in 4.2-4.4 ppm range. Four protons of the succinate segment are observed as a singlet at 2.6 ppm. A weak signal around 3 ppm must be due to CH_2 protons attached to OH group at the end of the chain. Integral ratio of this signal to that of the methyl protons at 1.9 ppm is about 2/15, which indicates a number average molecular weight of 1230 Da, whereas GPC indicates 1680 Da. In the spectra of the samples with few percent of GMA the typical double bond and methyl group signals of this component are not observable. However the typical signals of GMA located around 4.3 ppm are observed as broad bands. This is evidence of incorporation of GMA component in the structures.

The broad signal around 3,3 ppm (in fig.2) is associated with CH protons (attached to oxygens) of cyclohexanol units at the chain end. Based on the integral ratio of this signal to those of succinate protons at 2.6 ppm, number average-molecular weight was estimated to be 850 Da.

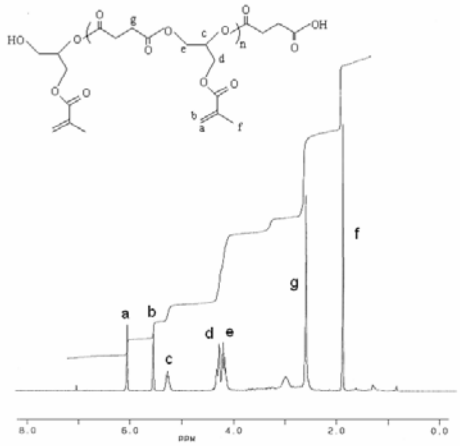


Figure-1: 1H-NMR spectrum of GMA-SA oligoester in $CDCl_3$ solvent.

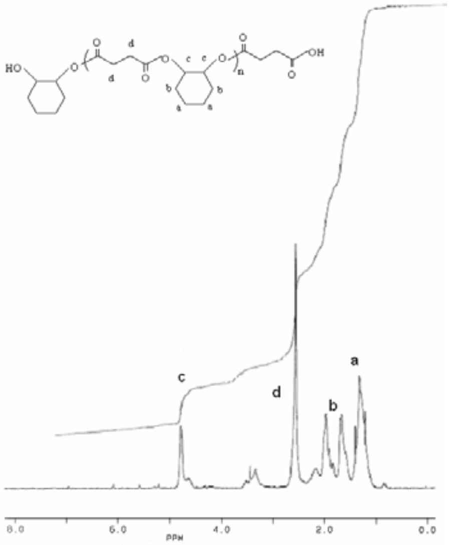


Figure-2: 1H-NMR spectrum of CHO-SA oligoester in $CDCl_3$ solvent.

Photocuring

IR spectra of the oligomers do not allow direct monitoring of acrylate double bond intensities to follow extent of the photo curing reactions. Because C = C stretching vibration at 1650 cm^{-1} is broadened with C = O stretching vibration band at 1730 cm^{-1} in the IR spectrum of the sample constituting with GMA component (Figure 3a), which is common for enone structures . Also carbonyl group vibration of the succinate component appears at the same position. Moreover olefinic C-H bending vibration at around 810 cm^{-1} is not well discernible. Because of this reason we have followed an alternative route for estimation of the double bond consumptions in photo curing. This route is based on different peak of the CHO-SA oligomer at 1565 cm^{-1}. Thus, in the IR spectrum of the CHO-SA oligomer (Figure 3b), integral ratio of the intensity of the

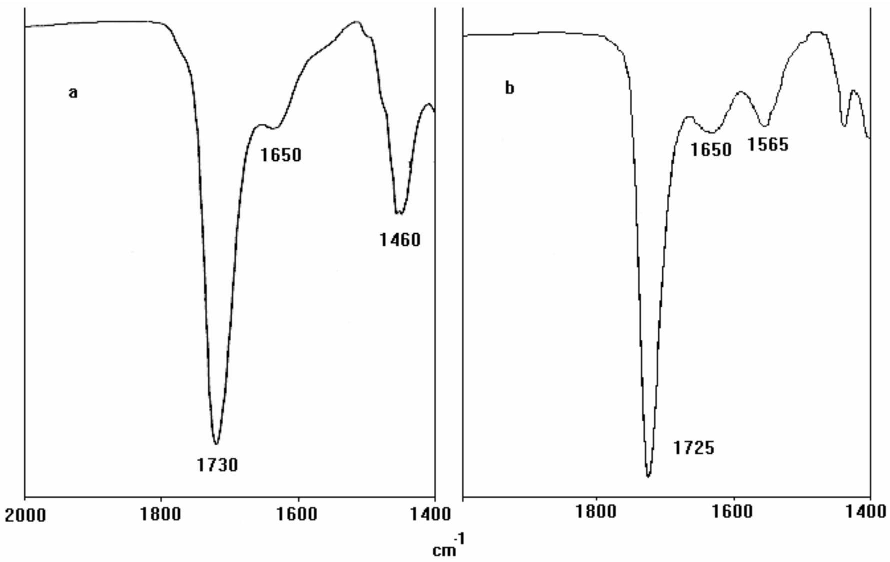


Figure-3: FT-IR spectra of oligoesters of GMA-SA (a) and CHO-SA (b) in 1400-2000 cm^{-1}.

bands in 1620-1750 cm^{-1} range to that of the band at 1565 cm^{-1} was designated as "a_o". The same integral ratio for the samples consisting of GMA was designated as "a".

The difference, a-a_o must be proportional to the double bond content. Indeed a-a_o versus molar GMA content gives nearly linear plot. Extents of the photocuring reactions were estimated by monitoring variation of a-a_o with exposure time. Experiment showed that in the thin films with 10 % GMA, about 75 % of the double bonds undergo photoreaction (Figure 4). Whereas, the films with less GMA component are somewhat slow in the photoreaction as expected.

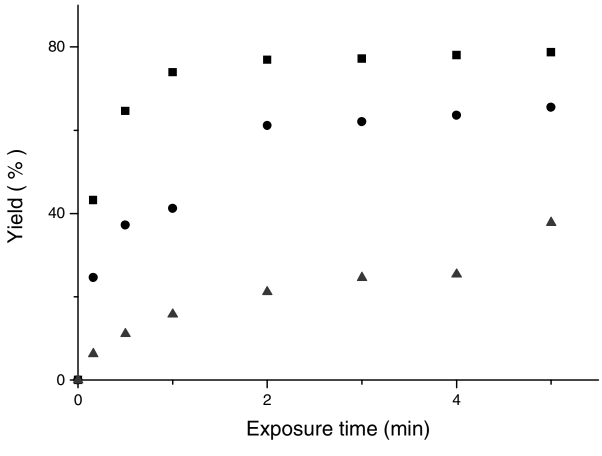


Figure-4: Conversion-exposure time plots of methacrylate double bonds in the photocuring of the oligoester films with 2 % GMA (▲), 5 % GMA (•), 10 % GMA (■).

In conclusion; reaction of GMA with SA forms low molecular weight polyesters with zinc succinate catalyst at 90 °C. The method presented offers a useful pathway for preparing oligoesters with methacrylate pendant groups. The double bond densities can be adjusted by partial replacing the GMA component with CHO. The resulting materials undergo photocrosslinking without using additional reactive comonomer.

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