

Novel photocurable polyethers with methacrylate pendant groups

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Abstract

A method for preparation of novel fast photocurable polyethers is described. Thus, novel polyether, poly(3-methacryloxy propylene oxide) was obtained in low molecular weights (M_n : 1700 Da) by cationic ring opening polymerization of the epoxy group of glycidyl methacrylate (GMA) in presence of trimethylsilyl triflate (TMSTF) as initiator. Copolymerization of the monomer with cyclohexene oxide (CHO) in the same reaction conditions yielded copolyethers with methacrylate pendant groups. A series of copolymers with various GMA contents (10–100% mol/mol) were prepared using CHO as diluting comonomer. ^1H NMR spectra showed that oxirane function of GMA is somewhat less reactive than CHO. Having methacrylate pendant groups the resulting waxy polymers underwent rapid photocrosslinking to give glassy hard materials upon UV irradiation at 350 nm, in the presence of benzoin as photoinitiator. Photocuring abilities of the copolymers were investigated by real time FT-IR using in dimethoxyethane solutions (14.7% w/w). The results showed that, 60% double bonds disappear within 150–300 s by irradiation of diluted copolymer solutions with Xenon lamp (150 W).

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1. Introduction

Radical-type photocurable polymers have found many applications in various fields such as microelectronics, coating, etc. Increasing demand on faster curability has led to a constant search for polymers photocrosslinkable in few seconds. Although various polymers with enone [1,2] and cinnamate [3,4] functions have been reported, acrylate containing polymers are mostly preferred due to well-known

reactivity of the acrylate double bond in radical polymerizations. Many acrylate-functionalized telechelics [5] and multifunctional monomers [6] with ether, ester, carbonate or silicone connecting units are now commercially available. For application viewpoint, polymers possessing fast polymerizable vinyl pendant groups are mostly preferred due to their easy manipulation.

There appear few reports on polymers with acrylate side groups. Modification of epoxidized polyisoprene with acrylic or methacrylic acids [7] and reaction of soluble phenol–formaldehyde resins with glycidyl methacrylate (GMA) have been demonstrated to be useful routes in preparing polymers

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with methacrylate pendant units [8]. However the polymer modification needs tedious processes and conversion yields depend on preparative conditions.

We have concluded that, the use of suitable bifunctional monomers having selectively polymerizable groups would be very useful in curing systems. Selective polymerization via one of the groups and followed crosslinking of the resulting polymer through the second group by another means seems to be an attractive strategy for efficient curing. Macromonomers carrying such a dual functionality have been subjected previously by Ito-Yagci group [9] and coined as “hybrid macromonomers”.

However, this requirement is rarely encountered in commercial bifunctional monomers. In this respect, GMA seems to be a suitable monomer having cationically polymerizable epoxy group and radically polymerizable methacrylate double bond.

Interestingly polymerization of this monomer via ring opening of the epoxy group has been subjected only in few papers. Yan and coworkers described synthesis of amphiphilic block copolymers by cationic ring opening of the epoxy group of GMA in presence of poly(ethylene glycol) [10].

Recently, we have described simultaneous ring opening of the epoxy group of GMA with succinic anhydride, yielding photocurable polyesters [11]. However, possible hydrolysis of the ester linkage involved might be undesirable for some applications.

Herein we report novel and hydrolytically stable polyethers with methacrylate pendant groups. This was achieved by ring opening copolymerization of oxirane group of GMA with cyclohexene oxide (CHO) using trimethylsilyl triflate (TMSTF) as cationic initiator. CHO was employed as diluting comonomer to adjust density of the methacrylate pendant groups.

2. Experimental

2.1. Materials

Trimethylsilyl triflate (Lancaster), benzoin (E. Merck) were used as purchased. Cyclohexene oxide (CHO) was purified by distillation over CaH_2 (38 °C/0.5 mm). In the polymerization process purity of the GMA monomer is crucial. Commercial GMA contains glycidol up to 5%. Removal of glycidol impurities prior to the copolymerization is essential to avoid the side reactions. In order to obtain glycidol-free monomer 50 mL of commercial

GMA was washed several times with 3% of aqueous NaCl solution (6 × 100 mL). Then it was dried with anhydrous MgSO_4 and distilled over CaH_2 in the presence of hydroquinone (0.2 g) at 98 °C/0.5 mm. Overall yield was 38 mL.

2.2. Instrumentation

^1H NMR spectra were recorded by Bruker AC250, 250 MHz spectrometer, with CDCl_3 as solvent. Gel permeation chromatography (GPC) traces of the copolyethers were recorded by Agilent 1100 equipped with refractive index-detector (Waters 410 Differential Refractometer) and Waters Styrogel columns: HR4, HR3, and HR2. THF was eluent, (0.3 mL/min), using polystyrene as standard. FT-IR spectra were recorded on a Perkin Elmer FT-IR Spectrum One B spectrometer.

2.3. Cationic polymerization

A typical procedure for the cationic copolymerization is as follows: for the bulk polymerization of GMA–CHO mixture (1/9 mol/mol), a 50 mL volume of three necked flask was equipped with a nitrogen inlet, vacuum connector and a rubber stopper. The system was dried by successive evacuation and nitrogen filling (5 times). The flask was charged with 9 mL (9×10^{-2} mol) CHO and 1.4 mL (10^{-2} mol) GMA under nitrogen flow. Then 0.1 mL (5.5×10^{-4} mol) trimethylsilyl triflate (TMSTF) was introduced through a hypodermic syringe while stirring. The flask was mounted on a continuous shaker and shaken for ten days at room temperature. The reaction content was poured into 60 mL methanol and the polymer precipitated was collected by filtering. The crude product was dissolved in 20 mL dimethoxyethane and reprecipitated in methanol (80 mL). Then it was washed with methanol (10 mL), and dried under vacuum at room temperature for overnight. Yield of the resulting polyether was 8.4 g (82.0%). Three copolyethers with different GMA molar ratios (10%, 20%, 30%,) were prepared by this procedure.

The same procedure was applied for homopolymerization of pure GMA, except cyclohexane was used for the precipitation.

2.4. Photocuring

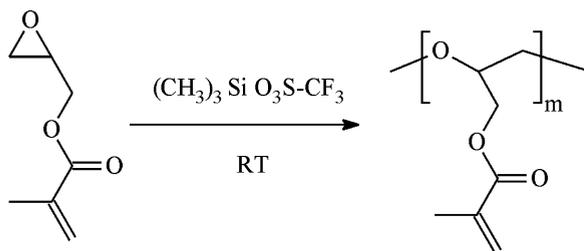
Photocuring abilities of the polyethers were investigated by real time FT-IR spectrometry, using

MVT model monochromatic fiber light source with Xenon lamp (150 W). In a typical procedure, 150 mg of polyether sample was dissolved in 1 mL dimethoxyethane solution of benzoin (10^{-2} M). One drop of this solution was placed on diamond surface in the cell holder. The FT-IR spectrometer was adjusted to transmittance mode and UV light beam was directed to the surface. The photocross-linking reaction was followed by monitoring variation of the strength of stretching vibration band of the methacrylate double bond at 1637 cm^{-1} .

3. Results and discussion

Cationic polymerization of glycidol-free GMA with TMSTF as initiator takes place via ring opening polymerization of the epoxy group involved (Scheme 1). Being liquid TMSTF is miscible with the monomers and does not bring any solubility problem. Although it has been used for cationic initiation in vinyl ether polymerizations [12], there appear no reports its use in polymerization of epoxides. Since polymerization with TMSTF is effected at room temperature, in this work, it was preferred as initiator. The bulk polymerization is very slow at room temperature, but proceeds smoothly to give viscous clear solutions. The reaction conducted for 240 h gave waxy polymer, poly(3-methacryloxypropene oxide) in 45% yield. Low molecular weight polymer ($M_n = 1700$ Da) so obtained is soluble in many organic solvents such as acetone, methanol, ethanol, and ether and insoluble in cyclohexane, *n*-hexane and water. In contrast to its copolymers with CHO, this polymer is also soluble in ethanol and methanol.

Obviously polymerization proceeds selectively via oxirane group of GMA yields soluble polymer due to non-polymerizability of the methacrylate double bond by cationic initiation. To avoid spontaneous polymerization of the methacrylate group by radical



Scheme 1. Polymerization of GMA via epoxy group by cationic ring opening.

mechanism, the reaction was carried out under oxygen-free conditions. ^1H NMR spectrum of the polymer (Fig. 1) shows untouched double bond proton signals as doublet at 6.1 ppm (*cis*-H) and 5.6 ppm (*trans*-H). The typical singlet of methyl group of the methacrylate unit appears at 1.9 ppm. The proton signals of COO-CH_2 , $-\text{CHO}$ and $-\text{CH}_2\text{O-}$ groups are observed respectively at 4.2, 3.7 and 3.4 ppm.

These results clearly indicate the polyether structure proposed. Having methacrylate pendant groups this polyether is very susceptible to spontaneous crosslinking and becomes insoluble within 5–6 h upon standing in the absence of inhibitor, at room temperature. Nevertheless the inhibitor-free polymer can be stored up to one week under nitrogen atmosphere in refrigerator.

3.1. Copolymerization

GMA also copolymerizes with CHO by cationic ring opening mechanism in the same reaction conditions (Scheme 2). Bulk polymerizations of the monomer mixtures with various GMA contents (10, 20, and 30 mol%) were carried out with 5.5 mol% TMSTF, at room temperature.

This procedure gave silky-white copolyethers in reasonable yields (68.3–82.0 wt.%) within 240 h of reaction periods (Table 1). Despite solubility of

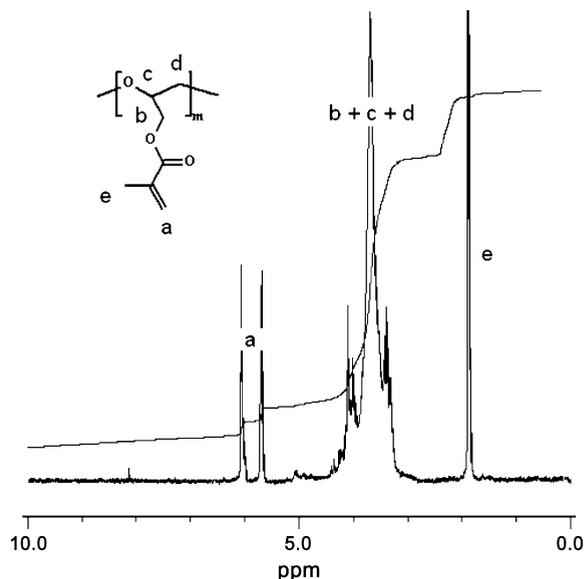
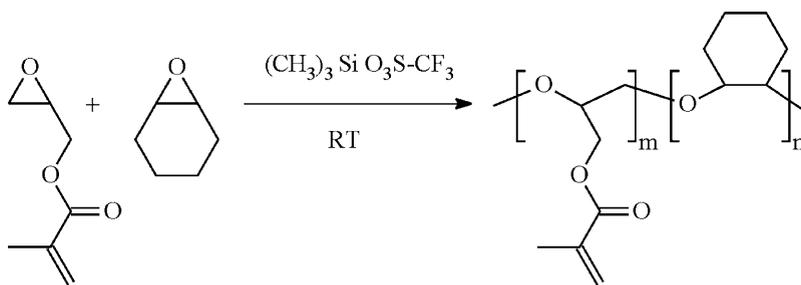


Fig. 1. ^1H NMR spectrum of the polyether obtained by cationic polymerization of GMA (in CDCl_3).



Scheme 2. Cationic ring opening copolymerization of GMA with CHO.

Table 1
Synthesis and photocuring characteristics of the polyethers

[GMA] ^a / [CHO]	Yield (%)	M_n^b	M_w	GMA ^c ratio (%)	Cure time ^d (s)
10/90	82.0	3950	6500	8.9	300
20/80	76.4	2700	4100	15.6	210
30/70	68.3	2300	3300	20.6	150
100/0	45	1700	2600	100	10

^a Molar ratio in the feed composition.

^b By GPC.

^c By NMR.

^d Time elapsed for disappearance of 60% of double bonds by irradiation in dimethoxyethane solution (14.7% w/w) at 350 nm.

the homopolymer in methanol, the copolymers were found to be insoluble in this solvent.

It was observed that, these copolymers are stable and can be stored in closed bottles. Gel permeation chromatography (GPC) traces of the copolyethers (Fig. 2) showed unimodal curves indicating formation of single macromolecular structures with low molecular weights ($M_n = 2300$ – 3950 Da).

It was observed that, both molecular weights and yields are reduced by increasing percentage of GMA in the feed composition. This can be ascribed to lower reactivity ratio of this monomer in the copolymerization.

FT-IR spectra of the polymers (Fig. 3) show typical stretching vibration bands of carbonyl and vinyl groups of the methacrylate pendant units at 1725 and 1637 cm^{-1} respectively. Intensities of these two peaks are proportional to GMA ratios in the feed compositions. This indicates existence of radically polymerizable methacrylate pendant groups in the copolyether structures.

In ^1H NMR spectra of the copolymers, characteristic double bond proton signals of the pendant methacrylate groups are observed as doublet at the same positions. Thus, in ^1H NMR spectrum of the polymer (Fig. 4) prepared from the mixture with

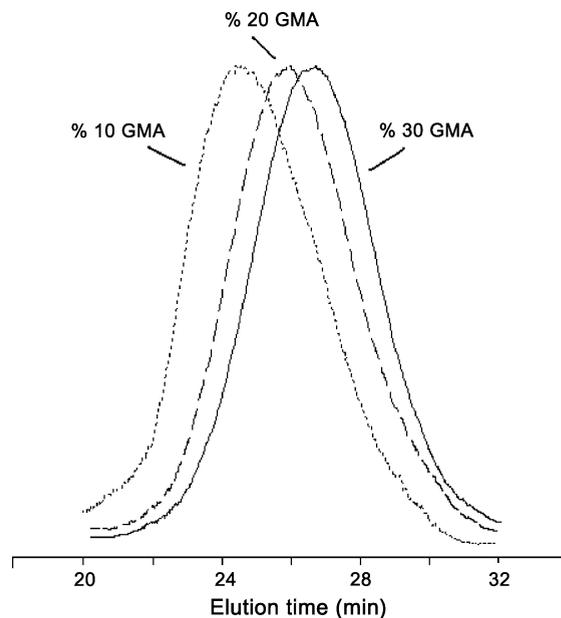


Fig. 2. GPC traces of the copolyethers (with THF as eluent, 0.3 mL/min).

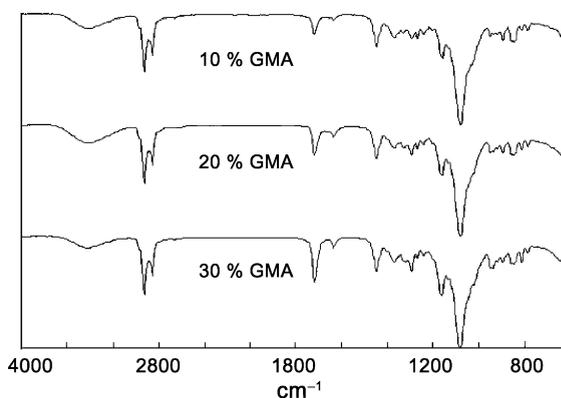


Fig. 3. FT-IR spectra of the copolyethers with various GMA contents.

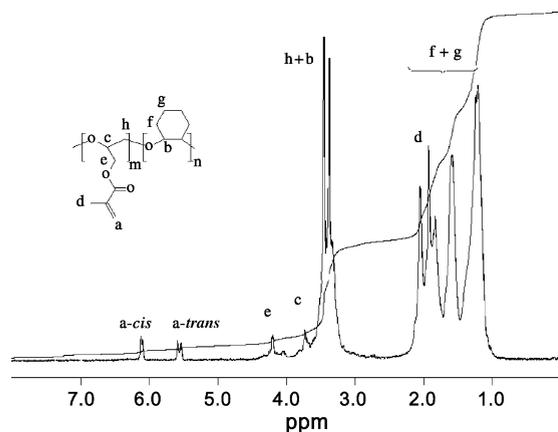


Fig. 4. ^1H NMR spectrum of the polyether (in CDCl_3) prepared with 20% GMA (mol/mol).

20 mol% GMA, the proton signals associated with methacrylate double bonds are observed at 6.1 and 5.6 ppm. Integral ratio of this doublet increases in accordance with increasing percentage of the GMA content in the polymerization mixture. This result reveals incorporation of GMA units into the polymers. Two protons of cyclohexane carbons linked to the oxygen atoms and propyleneoxy group protons of the GMA component give strong signals centered at 3.4 ppm. Methyl group protons of GMA unit and rest of the cyclohexane protons show strong multiplet in 1–2.1 ppm range.

Estimation of the copolymer compositions based on integral ratios of the double bond proton signals to those of the other protons indicate somewhat less GMA contents (see Table 1). For instance, integral ratio indicates a 15.6 mol% of GMA in the product obtained by polymerization of the mixture with 20% GMA. The copolymer composition data given in Table 1 can be used for simple estimation of the reactivity ratios of the monomers, based on so called “copolymer equation” [13].

$$F_1 = \frac{r_1 f_1^2 + f_1(1 - r_1)}{r_1 f_1^2 + 2f_1(1 - f_1) + r_2(1 - f_1)^2}$$

where, the subscript “1” denotes GMA monomer. F_1 and f_1 are molar ratios of this monomer in the copolymer and feed compositions respectively. Reactivity ratios of GMA and CHO are represented as r_1 and r_2 respectively. The equation can be rearranged to

$$\left(\frac{f_1}{1 - f_1}\right) \times \left(\frac{2F_1 - 1}{F_1}\right) = \left(\frac{f_1}{1 - f_1}\right)^2 \times \left(\frac{1 - F_1}{F_1}\right) \times r_1 - r_2$$

A plot of the left term versus coefficient of r_1 (Fineman–Ross plot) gives straight line with a good linear correlation factor ($R = 0.99969$). From the slope and intercept of the plot (Fig. 5) one finds; $r_1 = 0.34 \pm 0.008$ and $r_2 = 0.98 \pm 0.009$, indicating lower reactivity of the GMA component in the cationic copolymerization, as described above.

The copolymerization with CHO in different molar ratios provides a means of diluting effect on the methacrylate pendant group densities of the copolymers. In another words ratio of the diluting comonomer, CHO is important parameter to attain any desired cure time. Moreover such a cationic copolymerization with GMA seems to be applicable to ordinary epoxy compounds, which would be useful for preparing many photocuring formulations with tunable characteristics.

3.2. Photocuring of the polyethers

These polyethers are promising candidates as macromolecular crosslinker in photocuring processes. In practice these must be used in combination with an acrylic monomer as reactive diluent. In order to follow specific behavior of the pendant double bonds, in the present work we have not used an acrylic monomer as solvent in the photocuring experiments.

Photocuring abilities of the polyethers were investigated by “real time FT-IR” spectrometry technique. For this purpose the samples were irradiated at 350 nm in presence of benzoin (Type1 initiator) as sensitizer. Since the photopolymerization is extremely fast, in order to follow photocuring

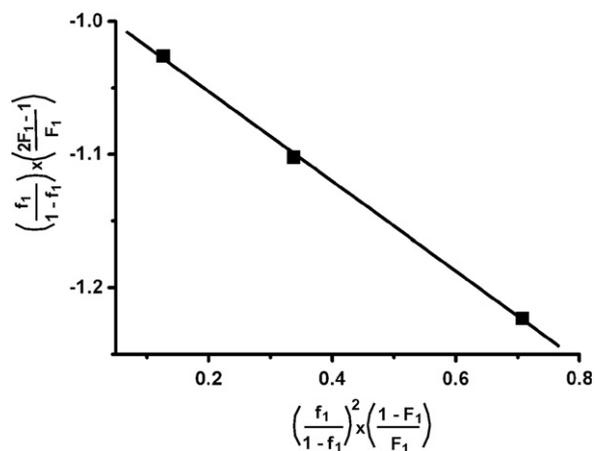


Fig. 5. Fineman–Ross plot for the cationic ring opening copolymerization of GMA with CHO.

behavior of the polyethers, the experiments were carried out with dimethoxyethane solutions (14.7% w/w) having 0.13–0.35 molar double bond concentrations. Extents of the photocrosslinkings were followed by monitoring the diminishing integral area of the C=C stretching vibration band of the methacrylate group at 1637 cm^{-1} . Conversions of the double bonds were simply estimated by the following relationship:

$$\% \text{ Conversion} = \frac{I_0 - I}{I_0} \times 100$$

where, I_0 is initial integral area of the band at 1637 cm^{-1} and I is the band intensity at any cure time. The band intensities were designated as the depth between the band maxima and the inflection point at the upper edge of the band, as shown in Fig. 6. This figure shows representative example for the decreasing intensity of the band at 1637 cm^{-1} by UV exposure.

The double bond conversions were calculated for each exposure time by using above formula and relevant data collected were used to build Fig. 7. The figure shows that the cure time is reduced greatly by the increasing GMA content. Photocrosslinking of the polyester obtained from pure GMA is extremely fast as expected. More than 60% of its double bonds disappear within 10 s of irradiation in dilute solution. For comparison of crosslinking abilities of the polyethers this level of conversion was chosen as reference point. Experiments showed that, in case

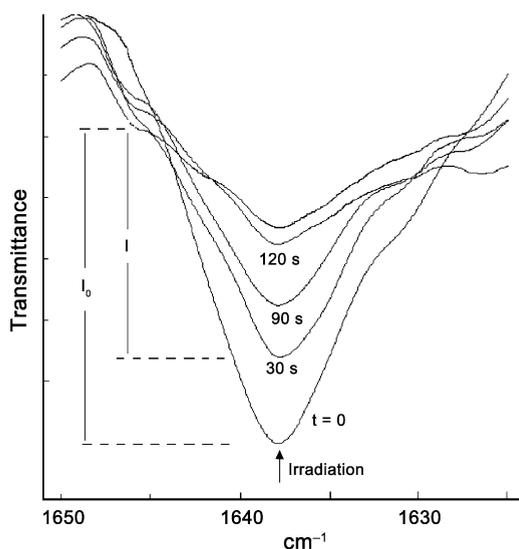


Fig. 6. Variation of the peak strength of the double bond with cure time, for the copolyether with 30 mol% GMA.

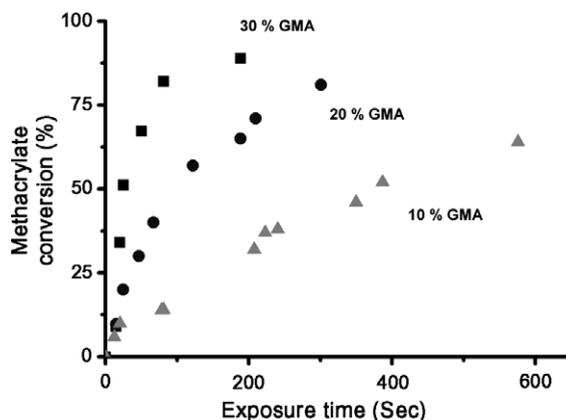


Fig. 7. Photocrosslinking profiles of the copolyethers in dimethoxyethane solutions (14.7% w/w) upon exposure at 350 nm.

of the copolymer with 30% GMA (20.6% estimated by $^1\text{H NMR}$) 60% double bond consumption is attained within 150 s of exposure time. Obviously density of the pendant vinyl groups, power of the light source and concentration of the photoinitiator are the main factors affecting on cure times.

One can conclude that photocuring of these polyethers can be performed in considerably shorter irradiation times. For instance, in coating applications of the copolyether with 30% GMA content, 20% of double bond consumption would be enough to attain satisfactory hardness. It seems to be possible that, such a hardness can be attained within 1 s by irradiation of more concentrated solutions with powerful lamps. Even shorter cure times may be possible by increasing GMA percentage of the copolymers. More important is that, copolyether samples stored in closed bottles for more than one month at room temperature were still soluble and their FT-IR spectra showed typical methacrylate double bond vibration at 1637 cm^{-1} .

4. Conclusion

In conclusion, cationic ring opening copolymerization of GMA with CHO yields poly(3-methacryloxy propylene oxide-co-cyclohexene oxide)s by initiation with TMSTF. Although the homopolymer of GMA has limited shelf life, its copolymers with CHO show reasonable stabilities. These novel polyethers seem to be promising materials for preparation of ultrahigh speed curing formulations. Elastomeric character of the polyethers and transparency of their thin films are the additional advantages. It seems to be more likely that, cationic copolymerization of GMA is not confined only to

CHO and the reaction is common for all epoxy compounds. Apparently this chemistry enables the preparation of many different polyether architectures by exchanging the comonomer, CHO with other epoxy compounds. Considering with those peculiarities the polyethers presented would be very useful in creating micro size patterns for microlithography, direct-writing technology and printed circuit boards.

Acknowledgement

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