

# Three-Component Terpolymers of Glycidyl Methacrylate with Good Swelling Characteristics

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**ABSTRACT:** Highly swellable glycidyl methacrylate terpolymers with styrene and a series of crosslinkers (divinyl benzene and ethylene, diethylene, and triethylene glycol dimethacrylates) were obtained by suspension polymerization. The loading capacities of the resins, their glass-transition temperatures, and their swelling characteristics in 20 solvents

were examined with respect to the monomer composition. A selected resin was modified for a cobalt-imine complex and tested as a catalyst in a model ring-opening reaction. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3800–3807, 2007

**Key words:** catalysts; copolymerization; gels; swelling

## INTRODUCTION

The free-radical polymerization or copolymerization of glycidyl methacrylate (GMA) provides polymers with epoxy groups. Further chemical modification of these groups opens a route to materials with diverse properties. For instance, GMA suspension copolymers are used as supports for enzymes<sup>1–3</sup> and as sorbents for chromatography.<sup>4–7</sup> They can also be used in removing metal ions or impurities from a solution (scavenger resins).<sup>8–14</sup> GMA polymers have been used as biomaterials as well, such as protein-separation and purification agents.<sup>15–17</sup> They can also act as biodegradable hydrogels for the controlled release of drugs.<sup>18,19</sup> Recently, functional polymers have attracted increasing interest as supports for catalysts.<sup>20–22</sup>

Low-crosslinked polymers obtained by suspension polymerization play a particular role in these applications. The catalytic activity of metal complexes immobilized on such supports can be comparable to the activity of homogeneous analogues because of the good swelling characteristics of the polymer matrix. Readily modifiable epoxy groups in GMA copolymers make these materials useful from this point of view as well.<sup>23–25</sup>

In this article, new three-component, low-crosslinked GMA terpolymers are described. Good swelling characteristics and loading capacities around 0.8–1.9 mmol of epoxy groups per gram make these resins interesting for their further chemical modification for

scavenger and catalytic applications, and this will be a subject of our future research.

## EXPERIMENTAL

### Materials

Aldrich (Steinheim, Germany) or Fluka (Buchs, Switzerland) supplied GMA (97%), styrene (S; 99%), triethylene glycol dimethacrylate (TEGDMA; 95%), diethylene glycol dimethacrylate (DEGDMA; 95%), ethylene glycol dimethacrylate (EGDMA; 98%), and divinyl benzene (DVB; a mixture of isomers, ~ 80%), which were purified by extraction with 5 wt % NaOH in a 20 wt % NaCl solution before use. Azobisisobutyronitrile (AIBN) was recrystallized from methanol (MeOH). Other reagents and solvents (diluent) obtained commercially were used as received from Aldrich, Fluka, or POCh (Gliwice, Poland).

### Resin synthesis

Three-component terpolymers, containing GMA, S, and DVB (or EGDMA or DEGDMA or TEGDMA), were obtained as microbeads in a typical suspension copolymerization procedure.<sup>26</sup> Resin syntheses were carried out under a nitrogen atmosphere in a 800-mL cylindrical reactor equipped with a heating coat, a mechanical stirrer, a reflux condenser, and an addition funnel. The initiator [AIBN or benzoyl peroxide (BPO); 1 wt %] was dissolved in monomers, and then the mixture was diluted with a mixed solvent (4/1 w/w cyclohexanol/*n*-octanol) taken in 1/1 (w/w) proportions. *n*-Decanol and *n*-dodecanol were also used in place of *n*-octanol. The dispersion medium was prepared through the dissolution of 1 wt % poly(vinyl pyrrolidone) (PVP; K90) in deionized water, and it was used in a 1/4 (w/w) ratio according to the

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organic phase. The reaction mixture was stirred at 350 rpm for 2 h at 70°C and then for 6 h at 80°C. After cooling, a washing procedure was applied to remove the diluents and any unreacted monomers from the products. The spherical beads that formed were decanted and washed many times with excess water, and then they were transferred to a Soxhlet apparatus, in which extraction with acetone for 6 h was carried out. After that, the microbeads were resuspended in MeOH and left in this solvent for 12 h. This procedure protected the beads from agglomeration during drying. Then, the copolymers were filtered out and dried *in vacuo* at 40°C up to a constant mass. The yield of the polymerization was calculated. The dry polymers were fractionated with sieves (250, 150, and 75  $\mu\text{m}$ ), and the yields of the fraction were determined.

### Resin characteristics

The epoxy group content in the beads was determined by a modification of Jay's method.<sup>27</sup> Samples of the copolymers were swollen for 24 h in a mixture of chloroform and 25 wt % tetraethylammonium bromide in a glacial acetic acid solution initially, and then they were titrated with 0.1M HClO<sub>4</sub> in a glacial acetic acid solution in the presence of crystal violet. A blank test was carried out simultaneously.

Glass-transition temperature ( $T_g$ ) measurements were performed via differential scanning calorimetry with a Toledo 822<sup>e</sup> calorimeter (Mettler Toledo, Switzerland) with Star<sup>e</sup> System software. The resins were heated from 30 to 300°C and then cooled to 30°C. This procedure was repeated twice. The rate of heating and cooling was adjusted to 10°C/min.

The resin morphology was estimated with a JEOL JSM-5500LV scanning electron microscope (JEOL, Japan) and a Motic SMZ-143 stereoscopic microscope (Speed Fair Co., Ltd., Hong Kong) with a digital camera.

The swelling of the resins was determined in the following way: 1 g of an appropriate dry resin was added to a 10-mL graduated syringe that was equipped with a polypropylene filter. An appropriate solvent was added. After swelling equilibrium was achieved, the excess of the solvent was removed with the plunger. The increase in the volume ( $\Delta V$ ) and the swelling ratio ( $S$ ) were calculated as  $\Delta V = V_s - V_d$  and  $S = V_s/V_d$ , respectively, where  $V_d$  is the volume of the dry resin and  $V_s$  is the volume of the swollen resin.

### Catalyst synthesis

The selected polymer (3) was reacted in turn (1) with ethylenediamine (EDA; 5 equiv) in an *N,N*-dimethylformamide (DMF) solution (for 20 h at 70°C), (2) with 3,5-di-*t*-butylsalicylaldehyde (3,5-di-*t*-BuSA; 2 equiv) in dichloromethane (DCM; for 24 h at room tempera-

ture), and (3) with a solution of cobalt(II) acetate (1 equiv) in a mixed solvent (1/3 v/v MeOH/DCM for 1 h at room temperature). After each step, washing with DCM and MeOH and drying of the resins under reduced pressure were carried out. The loading of the metal ions in the products was estimated from the cobalt-ion concentration in the solution after the mineralization of the samples of the final resin. Atomic absorption spectrometry (AAS) technique was applied. Nitrogen and Fourier transform infrared analyses of the resins were also performed. All modification steps were carried out in a reactor placed on a shaker.

### Catalytic tests

A small vial (5 mL) was charged with an equimolar mixture of acetic acid and epichlorohydrin (1 mL) and polymer catalyst 3.1 (1 mol %). The reaction mixture was stirred at 40°C. The reagent conversion was monitored by capillary gas chromatography analysis (HP-FFAP, polyethylene glycol-TPA modified capillary column). Before recycling, the catalyst was washed from the reagents repeatedly with MeOH and methylene chloride in turn three times and once more with MeOH and dried under reduced pressure.

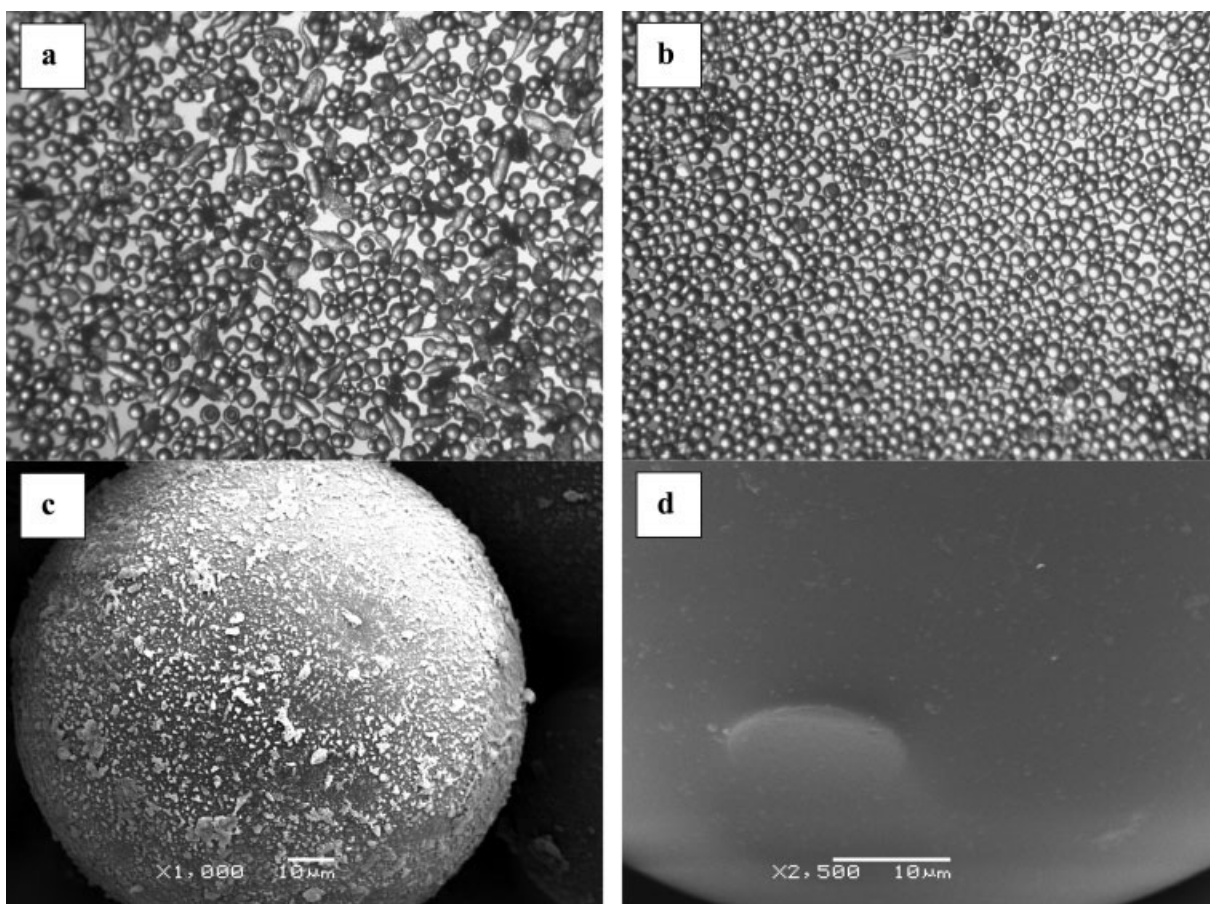
## RESULTS AND DISCUSSION

### Resin synthesis

Most references to GMA suspension copolymerization concern two-component systems, and only a few describe three-component terpolymers.<sup>26,28–36</sup> Highly crosslinked, macroporous resins are considered mainly in these publications. Moreover, from the published literature, it follows that a mixture of cyclohexanol and a higher linear alcohol, PVP, and AIBN are the most common diluent for monomers, suspension stabilizer, and polymerization initiator, respectively. Therefore, this system was employed first to obtain a low-crosslinked, three-component GMA terpolymer with S and DEGDMA. Unfortunately, a lot of defective particles, besides spherical beads, were formed in the presence of AIBN [Fig. 1(a,c)]. A better quality product was obtained when BPO was applied as the initiator [Fig. 1(b,d)]. Therefore, the last was used in all further experiments. Furthermore, using BPO made the bead surface less rough [Fig. 1(c,d)].

Four types of GMA resins were obtained (Scheme 1 and Table I). The concentration of the functional monomer was 10, 15, 20, or 30 mol %, and 2–5 mol % DVB, EGDMA, DEGDMA, or TEGDMA was applied as a crosslinking agent. S was used to dilute epoxy groups in the resin and to impart hydrophobic characteristics to the polymer matrix.

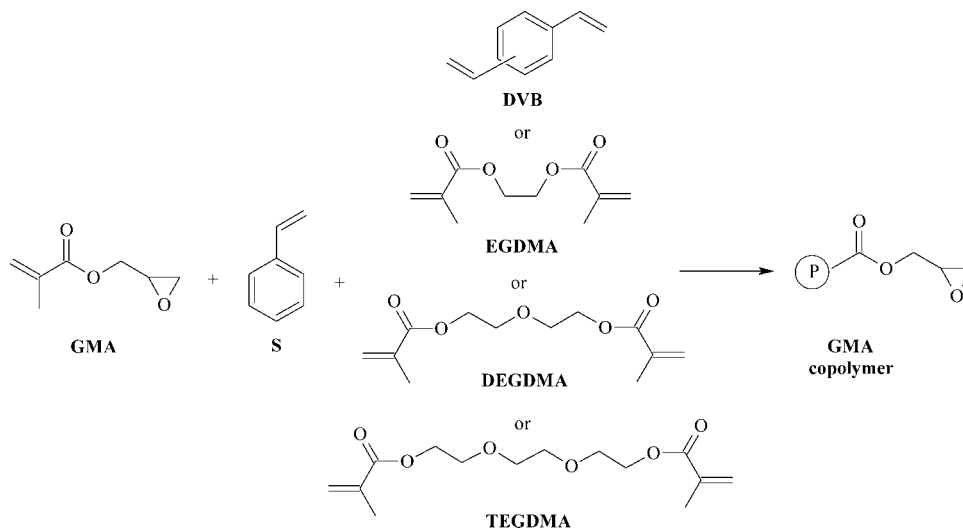
Most experiments were carried out in the presence of cyclohexanol/*n*-octanol (4/1 w/w) as a diluent of



**Figure 1** Influence of the initiator on the morphology of 20% GMA/3% DEGDMA/77% S resins: (a,c) AIBN and (b,d) BPO (the original magnification for parts a and b was 20 $\times$ ).

the monomers. The organic solvent was used in a 1/1 (w/w) ratio with respect to the monomers. Cyclohexanol/*n*-decanol and cyclohexanol/*n*-dodecanol (4/1 w/w) mixtures for diluting the reagents were also

tested. The quality of the products was then comparable. The applied copolymerization conditions yielded about 80% beads in the diameter range of 75–250  $\mu\text{m}$ .



**Scheme 1** Preparation of the GMA resins.

TABLE I  
Characteristics of GMA Resins

	Terpolymers	Yield [%]	Fraction 75–250 $\mu\text{m}$ [%]	Loading capacity of resin [mmol/g]		$T_g$ [ $^{\circ}\text{C}$ ]
				Calculated	Determined	
1	10%GMA-3%DEGDMA-87%S	72	79	0.89	0.77	107
2	15%GMA-3%DEGDMA-82%S	78	71	1.32	1.10	105
3	20%GMA-3%DEGDMA-77%S	80	77	1.73	1.43	110
4	20%GMA-2%DEGDMA-78%S	67	71	1.75	1.50	103
5	20%GMA-5%DEGDMA-75%S	83	87	1.69	1.28	109
6	20%GMA-3%EGDMA-77%S	80	84	1.75	1.38	110
7	20%GMA-3%TEGDMA-77%S	67	81	1.71	1.35	103
8	20%GMA-3%DVB-77%S	79	84	1.78	1.28	112
9	30%GMA-3%DEGDMA-67%S	84	66	2.51	1.92	109

### Loading capacity of the resins

Jay's method, which is often used to determine the epoxy group content in organic compounds, relies on the ring-opening reaction of oxiranes with HBr. The last is generated *in situ* from tetraethylammonium bromide during titration with an  $\text{HClO}_4$  solution in glacial acetic acid.

To apply this method to determine the loading capacity of our GMA resins, they were swollen for 24 h in a mixture of chloroform and 25 wt % tetraethylammonium bromide in a glacial acetic acid solution. After that, the beads were titrated with a solution of  $\text{HClO}_4$ . The long time of swelling was aimed at obtaining maximum access to the internal epoxy groups during titration. If the time of swelling had been too short, these groups could not have reacted completely, and the determination would have been flawed.

The loading capacities of the resins were 72–89% of the values calculated from the monomer composition, and they depended on the content of GMA in the feed (Table I). The differences between the calculated and determined epoxy group contents resulted from the lower availability of some internal epoxy groups for HBr molecules and from the differences in the chemical compositions of the copolymers in comparison with the initial monomer compositions. The latter was the result of the coefficients of reactivity of the monomers.

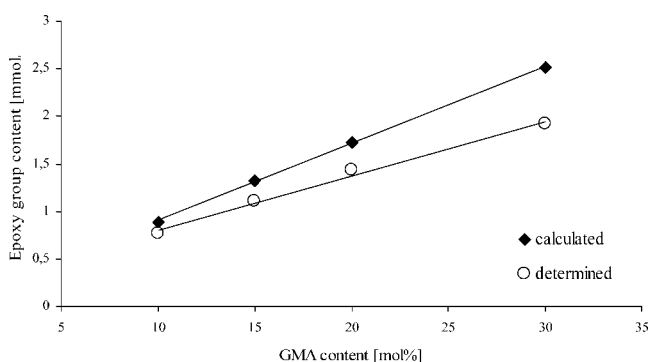


Figure 2 Epoxy group content versus the GMA content in GMA/3% DEGDMA/S resins.

The difference increased with an increasing amount of GMA in the monomer composition. The relation is illustrated in Figure 2 for the series of GMA/DEGDMA/S resins.

The difference between the calculated and determined epoxy group contents also increased with increasing polymer crosslinking (Fig. 3).

The effect of the nature of the crosslinkers on the loading capacity was found as well. Reducing the distance between the double bonds in the crosslinking agent, from DEGDMA to DVB, caused a rise in the difference between the calculated and determined epoxy group contents (Fig. 4). Theoretically, the GMA/TEGDMA/S resin should also fulfill this trend. However, the difference between the expected and determined loading capacity for this resin was similar to that of the GMA/EGDMA/S copolymer.

### $T_g$

$T_g$  is the one of the parameters that define the properties of polymers. The mobility of the polymer chains increases considerably above  $T_g$ , and the displacement of noncrosslinking polymer chains can take place. For crosslinked polymers, the movement of chains is limited by crosslinkers, which bond them together in a three-dimensional network. In the case of

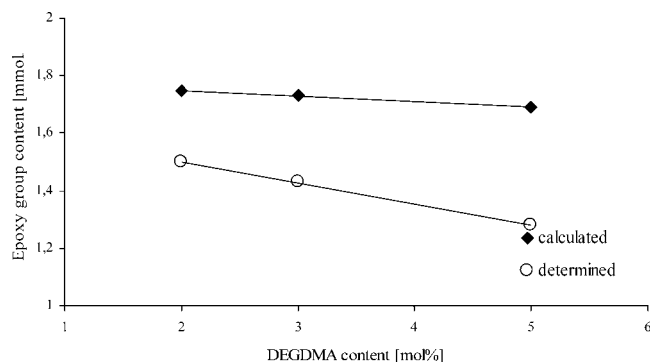
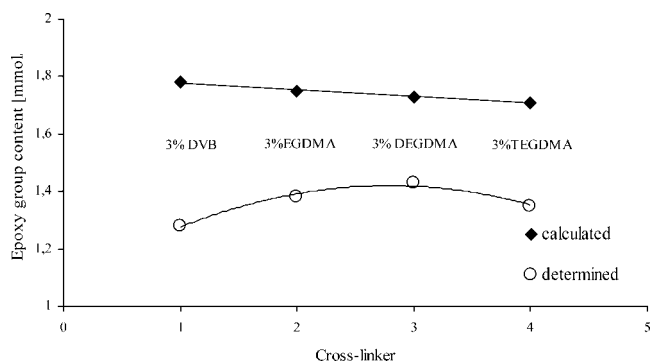


Figure 3 Epoxy group content versus the DEGDMA content in 20% GMA/DEGDMA/S resins.



**Figure 4** Epoxy group content in 20% GMA/3% cross-linker/77% S resins versus the nature of the crosslinker.

our three-component terpolymers, the average values of  $T_g$ , determined from heating and cooling curves, were in the range of 103–112°C (Table I).

Theoretically,  $T_g$  of copolymers should tend to increase with an increasing degree of crosslinking and with a decreasing distance between polymer chains, which is determined by a crosslinker. However, our results correlate with theoretical considerations only in the case of the structure of the crosslinkers (Table I).

## Swelling

In gel-type polymers, swelling is the main factor that determines access to internal functional groups.<sup>37</sup> In the dry state, the diffusion of even very small particles

through glassy polymer is very slow because polymer chains come into contact with one another. The interactions of resins with good solvents cause increasing network flexibility with increasing swelling.

Swelling, which causes increasing solvent porosity, makes the access of reagents to the inside of a polymer matrix possible. It allows molecules to penetrate and chemically explore the whole polymer network. Diffusion is the factor that determines the rate of reagent migration toward reactive sites in the matrix. Coefficients of diffusion should rise when the swelling degree of the resin increases because the time of the reaction performed on such a support will be shortened. Knowledge of the swelling characteristics allows us to select a solvent that will enable internal functional groups in the polymer network to react.

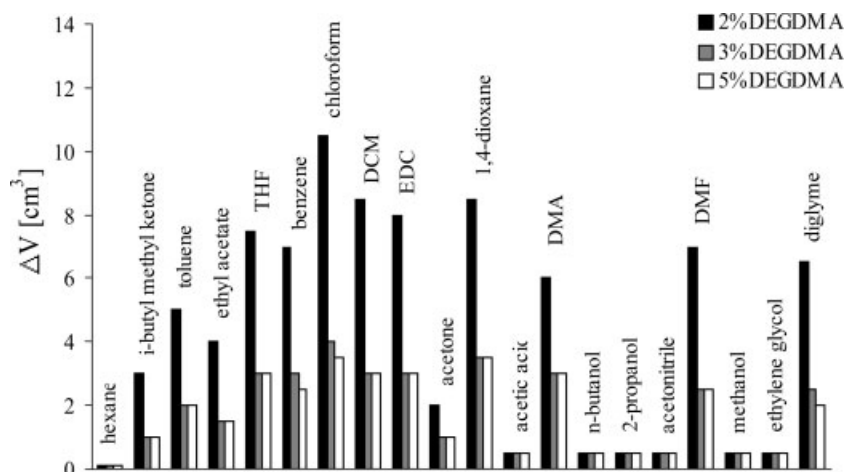
The method of measuring the swelling is essential for the obtained results. Measurements can be carried out in graduated cylinders or in syringes equipped with a filter. The volume of the swollen polymers is recorded in both ways. Syringes make the removal of excess solvent possible, and thus they provide more credible results. Griffith et al.<sup>38</sup> used the syringe method in their study of the swelling of some commercial resins in 39 solvents. The removal of excess solvent from the swollen resin is also the basis of the weight method of determining swelling. The growth of the polymer weight is used to calculate the solvent quantity closed off in a swollen polymer network.

We have studied the swelling of our copolymers in 20 common solvents. Because of difficulties in the

**TABLE II**  
Swelling Characteristics of GMA Resins

Solvent	$\delta$ , MPa <sup>1/2</sup>	Terpolymer							
		1	2	3	4	5	6	7	8
Hexane	14.9	0 (1.0)	0 (1.0)	0 (1.0)	0 (1.0)	0 (1.0)	0 (1.0)	0 (1.0)	0 (1.0)
<i>iso</i> -Butyl methyl ketone	17.2	1.5 (2.0)	1.5 (2.0)	1.0 (1.7)	3.0 (3.0)	1.0 (1.7)	1.5 (2.0)	1.0 (1.7)	0.5 (1.3)
Toluene	18.2	5.0 (4.3)	4.0 (3.7)	2.0 (2.3)	5.0 (4.3)	2.0 (2.3)	2.0 (2.3)	2.5 (2.7)	1.5 (2.0)
Ethyl acetate	18.6	2.5 (2.7)	2.5 (2.7)	1.5 (2.0)	4.0 (3.7)	1.5 (2.0)	1.5 (2.0)	1.5 (2.0)	1.0 (1.7)
THF	18.6	5.0 (4.3)	4.5 (4.0)	3.0 (3.0)	7.5 (6.0)	3.0 (3.0)	3.0 (3.0)	3.0 (3.0)	2.0 (2.3)
Benzene	18.8	5.0 (4.3)	4.5 (4.0)	3.0 (3.0)	7.0 (5.7)	2.5 (2.7)	3.0 (3.0)	3.0 (3.0)	2.0 (2.3)
Chloroform	19.0	7.0 (5.7)	6.0 (5.0)	4.0 (3.7)	10.5 (8.0)	3.5 (3.3)	4.0 (3.7)	4.0 (3.7)	2.5 (2.7)
DCM	19.8	5.5 (4.7)	4.5 (4.0)	3.0 (3.0)	8.5 (6.7)	3.0 (3.0)	3.0 (3.0)	3.0 (3.0)	2.0 (2.3)
1,2-Dichloroethane	20.1	5.5 (4.7)	5.0 (4.3)	3.0 (3.0)	8.0 (6.3)	3.0 (3.0)	3.5 (3.3)	3.5 (3.3)	2.0 (2.3)
Acetone	20.3	1.0 (1.7)	1.0 (1.7)	1.0 (1.7)	2.0 (2.3)	1.0 (1.7)	1.0 (1.7)	1.0 (1.7)	1.0 (1.7)
1,4-Dioxane	20.5	5.0 (4.3)	4.5 (4.0)	3.5 (3.3)	8.5 (6.7)	3.5 (3.3)	3.5 (3.3)	3.5 (3.3)	2.5 (2.7)
Acetic acid	20.7	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)
DMA	22.1	4.5 (4.0)	4.5 (4.0)	3.0 (3.0)	6.0 (5.0)	3.0 (3.0)	3.5 (3.3)	3.0 (3.0)	2.0 (2.3)
<i>n</i> -Butanol	23.3	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)
2-Propanol	23.5	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)
Acetonitrile	24.3	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)
DMF	24.8	4.0 (3.7)	4.0 (3.7)	2.5 (2.7)	7.0 (5.7)	2.5 (2.7)	3.0 (3.0)	2.5 (2.7)	1.5 (2.0)
Methanol	29.7	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)
Ethylene glycol	29.9	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)	0.5 (1.3)
Diglyme	–	3.5 (3.3)	3.5 (3.3)	2.5 (2.7)	6.5 (5.3)	2.0 (2.3)	3.0 (3.0)	2.5 (2.7)	1.5 (2.0)

<sup>a</sup>Per 1 g of the resin.



**Figure 5** Swelling ability of 20% GMA/DEGDMA/S resins in a series of solvents.

sedimentation of some swollen polymers in cylinders, we decided to use the syringe method.

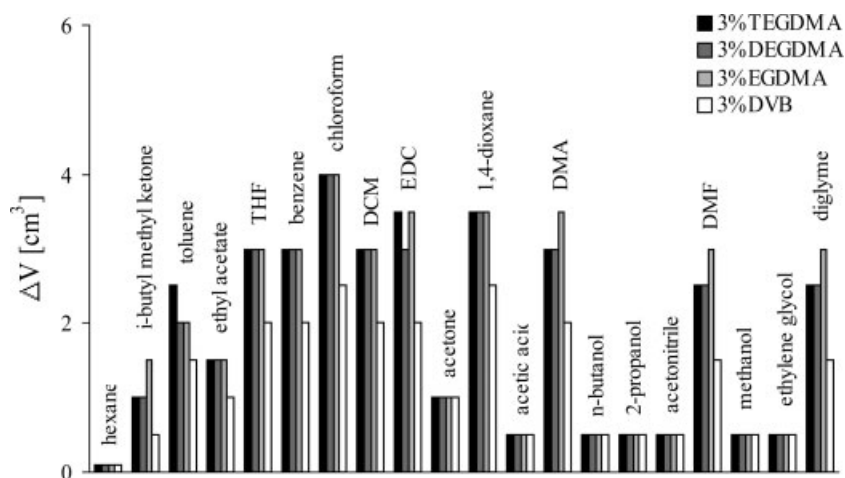
The results have shown that, after swelling, not only is copolymer volume growth a function of the solvent nature but the composition of the polymer matrix also plays a role (Table II). Theoretically, the mutual affinity of the polymer and solvent, which can be defined by the compatibility of Hildebrand's solubility parameters ( $\delta$ ),<sup>39</sup> should be an essential factor for swelling of resins.  $\delta$  for polystyrene is equal to about  $18 \text{ MPa}^{1/2}$ .<sup>39</sup> Therefore, in the case of our polymers, which contain S as a main monomer, we could expect the best swelling in solvents with  $\delta$  close to  $18 \text{ MPa}^{1/2}$ .

Among the solvents, toluene, ethyl acetate, tetrahydrofuran (THF), benzene, and chloroform belong to the group with  $\delta$  values within  $18\text{--}19 \text{ MPa}^{1/2}$ . The results show that all of them fulfilled the mentioned dependence. However, *i*-butyl methyl ketone, with  $\delta = 17.2 \text{ MPa}^{1/2}$ , turned out to be bad solvent. More-

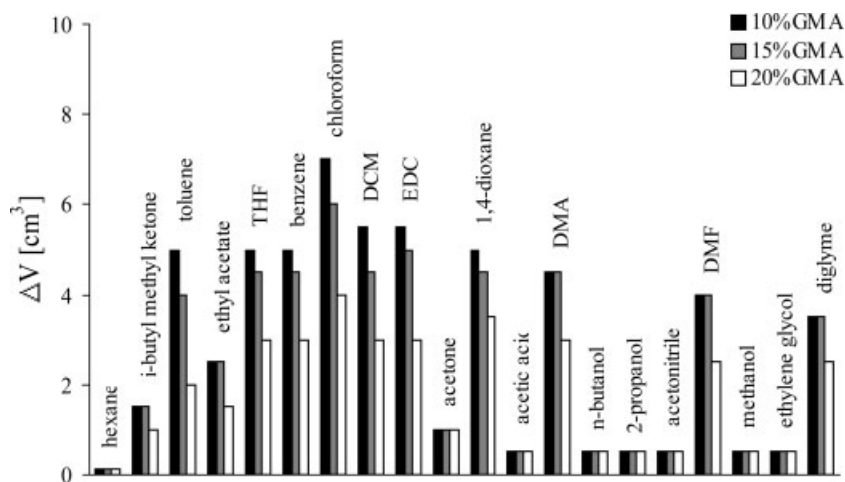
over, DCM, 1,2-dichloroethane (EDC), and 1,4-dioxane can also be numbered among the good solvents, although they have a somewhat larger  $\delta$  value. On the other hand, acetone and acetic acid have  $\delta$  values similar to that of 1,4-dioxane, but they are bad solvents for our copolymers. Furthermore, amide solvents, such as DMF and *N,N*-dimethylacetamide (DMA), with  $\delta$  values substantially different from those mentioned, strongly swell our resins (Table II).

Depending on the swelling degree, the solvents can be divided into several groups. Chloroform turned out to be the best of the applied solvents. 1,4-Dioxane, EDC, DCM, THF, benzene, DMA, DMF, diethylene glycol dimethyl ether (diglyme), and toluene also swelled the resins strongly. In ethyl acetate, *i*-butyl methyl ketone, and acetone, the copolymers clearly swelled less. Hexane, acetonitrile, acetic acid, and alcohols did not swell them.

According to expectations, the swelling ability decreases with the crosslinking of the resins (Fig. 5).



**Figure 6** Swelling ability of 20% GMA/3% crosslinker/77% S resins in a series of solvents.



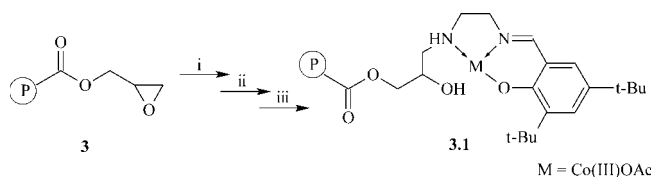
**Figure 7** Swelling ability of GMA/3% DEGDMA/S resins in a series of solvents.

Theoretically, the ability to swell should rise with increasing distance between the polymer chains, which is determined by a crosslinker (i.e., from DVB to TEGDMA). However, our results do not correlate in this way (Fig. 6).

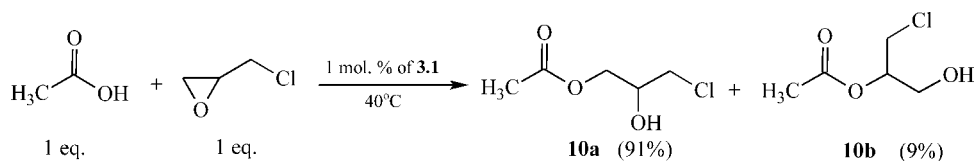
Increasing the GMA content in the polymer matrix generally reduces its swelling (Fig. 7).

### Resin application

The swelling ability of GMA resins in common organic solvents makes their chemical modification easy. Our experiments carried out with the selected resin have shown that a new amine resin with about 2.2 mmol of N/g can be obtained in the reaction with EDA in DMF.<sup>40</sup> The resin after swelling in DMF, DCM, and THF reacts readily with isocyanates, acid chlorides, and aldehydes.<sup>41</sup> Therefore, it can be used



**Scheme 2** Catalyst synthesis: (i) EDA (5 equiv), DMF, 70°C, and 20 h; (ii) 3,5-di-*t*-BuSA, DCM, room temperature, and 24 h; and (iii) Co(OAc)<sub>2</sub>·4H<sub>2</sub>O, DCM/MeOH (3/1 v/v), room temperature, and 1 h.



**Scheme 3** Model ring-opening reaction.

as a scavenger for removing these substances from organic solutions.

Chemical modifications of amine resins can deliver further reactive materials, such as supports for catalysts. According to the sequence of reactions presented in Scheme 2, cobalt-imine complex **3.1** (0.8 mmol of Co/g) was obtained.

The complex was preliminarily tested as the catalyst of the ring-opening reaction of epichlorohydrin by acetic acid (Scheme 3). It was recycled twice without sufficient loss of the activity (Fig. 8). In the presence of **3.1**, regioisomeric esters **10a** and **10b** were formed in a ratio of about 9/1.

### CONCLUSIONS

Highly swellable epoxy-functionalized resins with a loading capacity of 0.8–1.9 mmol/g are formed in suspension polymerizations in the presence of BPO as an initiator and a 1 wt % solution of PVP in water as a dispersion medium when a mixture of cyclohexanol and *n*-octanol (4/1 w/w) is used as a solvent for GMA/S/DVB (or EGDMA or DEGDMA or TEGDMA) monomer compositions. The resins swell strongly in chloroform, 1,4-dioxane, EDC, DCM, THF, benzene, DMA, DMF, diglyme, and toluene and moderately in ethyl acetate, *i*-butyl methyl ketone, and acetone. This might be advantageous for many chemical transformations leading to the synthesis of new materials, such as scavengers and supports for catalysts.

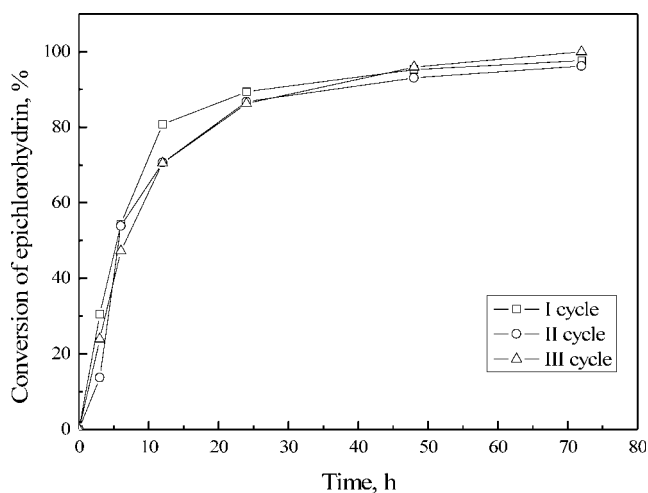


Figure 8 Results of the catalytic tests.

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