

# Preparation of 3-dimensional skeletal polymer via control of reaction-induced phase separation in epoxy/poly(ethylene glycol) blends

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## Summary

In order to prepare 3D skeletal polymer with low cross-linking density and high hydrophilicity bisphenol A epoxy was cured with diethylenetriamine in the PEG1000/PEG2000 mixing medium. The reaction-induced phase separation of this system was controlled by changing the weight ratio of PEG1000 and PEG2000. The morphology observation of the resulted polymers showed that the connectivity of epoxy phase strongly depended on the content of PEG2000 and was also influenced by the curing temperature. A 3D skeletal polymer with well-controlled macro-through-pores was prepared by using a mixture of PEG1000 and PEG2000 in 7/1 weight ratio as reaction medium and porogen. A unique light-filtrating effect was found in the prepared 3D skeletal polymer that filled with high refractive liquids. The effect most likely resulted from a total reflection mechanism of light in 3D macro-through-pores.

## Introduction

Phase separation in amorphous and even microcrystalline polymer blends occurs primarily by spinodal decomposition(SD)[1]. The necessary displacement into the spinodal region of the phase diagram can take place by polymerization of a monomer when the polymer being formed is incompatible with one or more of the other components in the system. This mechanism is known as reaction-induced phase separation (RIPS)[2,3] and has been extensively studied [4-15].

Polymerization and phase separation occur simultaneously during RIPS, and the coupling and competition of these two non-equilibrium phenomena determine the morphology of the final product. Inoue et.al. studied the morphology development via RIPS in epoxy/poly(ether sulfone) (PES) blends[14], the spherical domain structure was observed in a non-reactive PES system, and a bicontinuous two-phase structure was obtained when reactive PES with amine chain ends was used. It has been suggested that the SD induced by the cure reaction is suppressed and structure coarsening is delayed by the in situ formation of PES-epoxy block copolymer, so that the phase-separated structure can be fixed at an early stage of SD. Recently, Hosoya

et. al. carried out polycondensation reactions with an epoxy compound(bisphenol A diglycidyl ether) and an amino compound(4,4'-methylene-bis-cyclohexylamine) in low molecular weight poly(ethylene glycol)(PEG) mediums[16], 3D skeletal monolithic polymers were obtained and macro-through-pores could be found in the final products after the removal of PEG by water. According to the structure of curing agent and the mole ratio of the epoxy resin and curing agent (nearly 3/1), it was a highly cross-linked polymer with relatively low hydrophilicity. Polymer-based skeleton and macroporous monoliths have been used as the separation media in high-performance liquid chromatography(HPLC), those polymer-based monoliths realize good separation efficiency with low column pressure drop due to a combination of micron size polymer skeleton and relatively large macro-through-pores[17-20].

The preparation of 3D skeletal polymer with low cross-linking density and high hydrophilicity is a motive for the current work. Low cross-linking density may result in a flexible polymer with good mechanical strength, which makes the polymer more suitable for many applications. High hydrophilicity is usually important for the use of 3D skeletal polymer as a media in separating water-soluble organic substance. Obviously, to prepare such a 3D skeletal polymer it was necessary to explore a new RIPS system in which high molecular weight PEG should be used as reaction medium to produce SD. In this paper, we report a simple, efficient and green method to prepare a new 3D skeletal polymer via the control of RIPS in the curing reaction systems of bisphenol A epoxy in different PEG1000/PEG2000 mixing mediums. By using diethylene triamine as a hydrophilic curing agent the obtained 3D skeletal polymer showed strong hydrophilicity bearing a lot of functional groups. Furthermore, the mole ratio of epoxy resin and curing was adjusted to be 1/1, which yield a low cross-linking polymer having a flexible feature and good mechanical strength. In addition, we first time report an interesting opticle property of the prepared 3D skeletal polymer, the opaque solid turns into transparent as soon as the macro-through-pores in the polymer matrix are filled with highly refractive liquids.

## Experimental

### *Materials*

The epoxy resin used in this work is diglycidyl ether of bisphenol A with an epoxide equivalent weight of 185~210, supplied by Wuxi resin Co., China. Diethylenetriamine is of chemically pure grade and was used as the curing agent, purchased from Shanghai Reagent Co., China. PEG1000 (M=950~1050) and PEG2000 (M=1900~2100) were purchased from Shanghai Reagent Co., China.

### *Curing of epoxy resin*

A mixture of Epoxy resin(16.0g) and PEG(32.0g, totally) was heated and stirred to form a clear solution. Then the curing agent diethylenetriamine(4.0g) was quickly added with strong stirring. At the beginning of polymerization the reaction system kept homogeneous without any phase separation. The solution was poured into a polytetrafluoroethylene vessel and the reaction system was kept at the prescribed temperature in an oven for 3 hours. After curing, the sample was soaked in water for several times before PEG was completely removed from the polymer matrix. The white sample was dried completely in vacuum at room temperature for 2 days.

### *Morphology observation*

The cured sample was fractured at liquid-nitrogen temperature and the fractured surface was observed by scanning electronic microscopy (SEM)(JSM-T220, JEOL).

### *Absorption spectra and refractive index*

The absorption spectra of 3D skeletal polymer filled with high refractive liquids were recorded with a spectrophotometer using the corresponding liquids as references. One piece of polymer sample (3mm×8mm×25mm) was soaked in the first liquid, after measurement it was washed with cyclohexane followed by drying in the air at room temperature. It was then soaked in the next liquid to record another absorption spectrum. The refractive indexes of commercial divinylbenzene (DVB, 80wt% content), diphenyl ether, styrene and epoxy resin before cure were measured with an Abbe refractometer at 20°C. The standard method(ASTM D542-90) was used for the index of refraction of transparent polymer from cure of epoxy resin with diethylenetriamine in 4/1 weight ratio.

## **Results and Discussion**

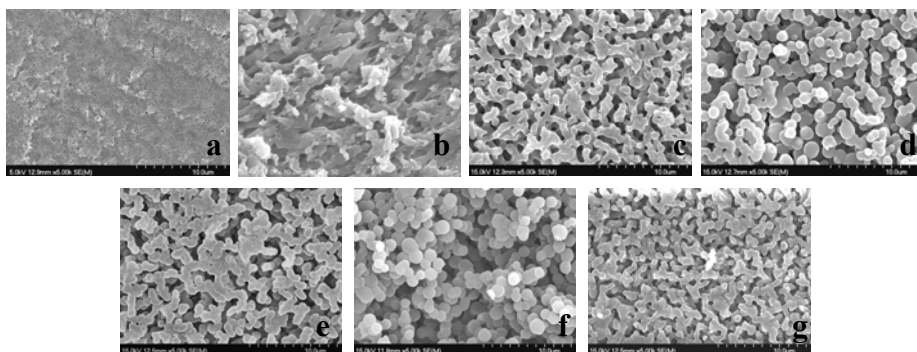
The melt points of PEG1000 and PEG2000 are in the range of 35~40°C and 48~52°C, respectively, while the curing temperature in the current work is above 60°C, therefore both kinds of PEG are in liquid state without any crystallization in all reaction systems. The epoxy resin before curing has good solubility in the melted PEG1000 and PEG2000. At the beginning stage of curing reaction the mixture was homogeneous. As the curing reaction proceeded, the molecular weight of the epoxy resin increased and the phase separation took place via SD, the transparent liquid gradually turned white and finally an elastic solid formed. The RIPS was found to be dependent on the difference of polarity between the resulted polymer and the reaction medium. As mentioned above the polymer is highly hydrophilic, thus a lower polarity of PEG medium is necessary for phase separation. For example, in a low molecular PEG medium such as PEG400 no phase separation was observed, the ample hydroxyl end groups increased the polarity of PEG medium. The RIPS appeared as long as the molecular weight of PEG was above 800, a higher molecular weight of PEG corresponds a lower concentration of end group, and therefore a lower polarity. In addition, the phase separation reappeared in PEG400 medium when 5wt% of LiCl was added to further-step increase its polarity.

Table 1 lists 7 different conditions for curing reactions in PEG medium. The total amount of PEG was fixed at 32g and the ratio of PEG1000 and PEG2000 was adjusted. Figure 1 shows the SEM micrographs of samples listed in Table 1. Sample **a** was prepared in the pure PEG1000, a full connectivity of epoxy phase can be seen from the morphology shown in Fig.1(a). Only very small pores left in the polymer matrix. It can be deduced that the rate of phase separation has been overwhelmed by that of curing reaction, as a result, the demixing at the early stage of SD was suppressed by the polymerizing and cross-linking in epoxy phase. Sample **b** was prepared in a mixture of 29g of PEG1000 and 3g of PEG2000. Macropores can be seen in the morphology shown in Fig.1(b), and the connectivity of epoxy phase was interrupted as compared to the case of sample **a**, however, the phase separation developed not efficiently for the linking up of macropores. Sample **c** and **d** were prepared in

**Table 1.** Polymerization condition

condition	sample	PEG1000(g)	PEG2000(g)	temp(°C)									
1	a	32	0	60									
2	b	29	3	60									
3	c	28	4	60									
4	d	26	6	60									
5	e	0	60	6	f	0	32	70	7	g	0	32	80
6	f	0	32	70									
7	g	0	32	80									

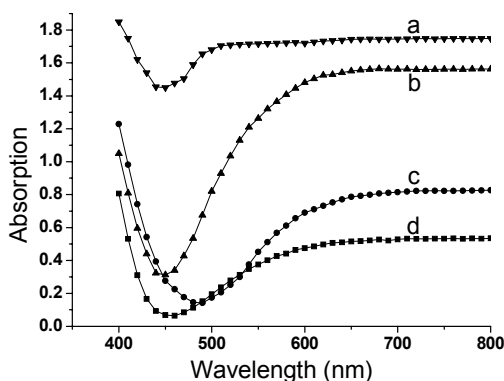
conditions differed very slightly with the condition 2, but the resulted structures were considerably changed by phase separation. Sample **c** shows a typical 3D skeletal structure with uniform macro-through-pores, while sample **d** shows an adhered particle structure. Obviously, a small portion of PEG2000 in the mixture could change the balance of curing and demixing. The connectivity of epoxy phase was greatly interrupted by the addition of PEG2000 although in low content in the mixing medium. From sample **d** to **e** the morphology changed very little as more amount of PEG2000 replaced PEG1000 in the reaction mixture. Sample **e** shows an interconnected globule structure resembling that of sample **d** except that the connectivity of epoxy was further-step interrupted.

**Figure 1.** SEM micrographs of sample a-g after removal of PEG

The connectivity of epoxy phase can be recovered by raising the curing temperature. Sample **f** and **g** were prepared in the same composition of reaction mixture as used for sample **e** but at different curing temperatures (listed in Table 1). An increasing tendency of the connectivity of epoxy phase can be seen from Fig.1(e) to Fig.1(g), indicating that the rate of curing was speeded up more effectively than that of phase separation by raising the reaction temperature. Sample **g** and **c** have a similar morphology except that the size of pore in Fig.1(c) is a little bit larger than that in Fig.1(g). The above results illustrated that the RIPS can be finely controlled by adjusting the molecular weight of PEG medium and the curing temperature. Based on the fact that a slight change of the content of PEG2000 gave rise to a remarkable effect on the phase separation, it was not reasonable to ascribe the effect to the viscosity increasing of reaction mixture. Our experimental results also showed that PEG6000 was more effective than PEG2000 to change the structure of epoxy phase.

Only 1/3 portion of PEG6000 produced the same effect as did by one portion of PEG2000. It has been clear that higher molecular weight PEG will produce stronger demixing tendency with epoxy phase. However, a clear mechanism is still unknown regarding the effect of small amount of high molecular weight PEG on the morphology of epoxy phase.

An interesting opticle phenomenon has been found from the 3D skeletal polymer. The original white polymer of sample c turned into transparent and blue-colored solid as soon as it was filled with DVB. The same phenomenon could also be observed if the polymer was soaked in diphenyl ether or a mixture of diphenyl ether and styrene in a volume ratio of 3/1. The transparent solid would return into opaque as it was put back to solvents such as cyclohexane, ethyl ether and methanol. It should also be noted that due to high hydrophilicity the polymer is not swollen in these low polar liquids at all. Fig.2 shows the visible spectra of the same piece of skeletal polymer filled with different liquids.



**Figure 2.** Visible spectra of sample c filled with styrene (a), a mixture of styrene and diphenyl ether in 1/3 volume ratio (b), diphenyl ether (c) and DVB (d)

It can be seen that every spectrum has a minimum absorption in blue area (450~500 nm). These are opticle windows from which the light can pass through the skeletal polymer to gave a transparent and blue-colored appearance. In general the absorption value increases in a sequence of DVB < diphenyl ether < mixing liquid < styrene, which is corresponding to a decreasing sequence of refractive index, DVB (1.580) > diphenyl ether (1.578) > mixing liquid of diphenyl ether and styrene (1.570) > styrene (1.546). A higher refractive index of the infiltrated liquid corresponds to a higher transmissivity of the solid. The skeletal polymer looks the most transparent in DVB and opaque in styrene. We believe that the effect has nothing to do with ordinary light scattering, the most reasonable explanation that we can find is the total reflection effect of light in 3D macro-through-pores. Firstly, all liquids that make the polymer transparent have high refractive indexes. The refractive index of epoxy resin was reported to be 1.567 before cure and 1.586 after cure by using a small amount of benzyldimethylamine as initiator of the anionic polymerization [21]. In the current curing reaction the weight ratio of epoxy resin and amine is 4/1, although the refractive index of epoxy resin was measured to be 1.568 (very close to the reported value), an excess of amine (a liquid with low refractive index of 1.481) used for cure led to a low refractive index of 1.566~1.567, lower than those of liquids used except

styrene. In the 3D skeletal polymer the real density of polymer may slightly lower than that of the same polymer in bulk size, the refractive index of 3D skeletal polymer will not be higher than the measured value (1.566~1.567). Secondly, the unswelling feature of the polymer in these liquids ensure a stable solid/liquid interface, which is another necessary condition for total reflection. In a total reflection situation the light conducting will be confined to macro-through-pores. Since the pore size is limited, the short wavelength light might be easier to pass through macro-through-pores than those with long wavelength, as a result, the white light would be separated by the light-filtrating effect and blue color appeared on the polymer samples. It can also be seen that the absorption spectra of the transparent samples are quite different although the refractive index of the infiltrated liquid differed very slightly, which might be owing to the different physical state of solid/liquid interfaces. Due to the low index of refraction of styrene the polymer filled with styrene is opaque, however, the absorption minimum can also be seen on the spectrum. Probably the total reflection has not completely disappeared in such a condition. It is the first time to report such an optical phenomenon from a 3D skeletal polymer, we tried to explain this phenomenon based on a total reflection mechanism of light in 3D macro-through-pores, however, some detailed aspects on physical principle are going to be investigated.

## Conclusions

The RIPS in the curing system of bisphenol A epoxy with diethylenetriamine in PEG1000/PEG2000 mixing medium has been studied and the control of phase separation has been realized by simply adjusting the weight ratio of PEG1000 and PEG2000. The connectivity of epoxy phase can be interrupted as the increase of amount of PEG2000 and recovered by raising the curing temperature. A 3D skeletal polymer with well-controlled macro-through-pores was prepared by using a mixture of 28g of PEG1000 and 4g of PEG2000 as reaction medium and porogen. A unique light-filtrating effect was found in the prepared 3D skeletal polymer that filled with high refractive liquids. The effect most likely resulted from a total reflection mechanism of light in 3D macro-through-pores.

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