Optical Properties of Transparent Resin Containing Barium Ion

Quan Lin, Bai Yang,* Yugang Ma,[†] Xuesong Meng, and Jiacong Shen[††]
Chemistry Department, Jilin University, Changchun 130023, P. R. China
[†]Physics Department, Jilin University, Changchun 130023, P. R. China
[††]Key Laboratory of Supramolecular Structure and Spectroscopy, Jilin University, Changchun 130023, P.R. China

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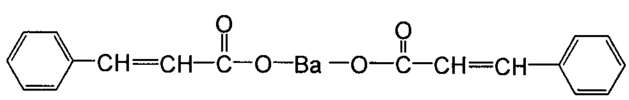
Barium ion (Ba^{2+}) was introduced into the transparent resins by copolymerization. The phase diagram of the transparency of the Ba^{2+}-containing polymer in a three-component system was determined and discussed. The Ba^{2+}-containing optical resins with good visible light transparency almost absorb X-ray completely and absorb γ-ray partially, as well as exhibit good optical properties and thermal stability.

People paid more attention to transparent resins because of the excellent properties of the materials such as lightness, impact resistance, and processability.[1,2] With the extensive usage of various radiation, there has a great interest in the preparation of radio-protective materials, especially in the study of the transparent radio-protective polymer.[3–5] The heavy metals (such as Pb, Ba, Ti, etc.) usually play a role in absorbing radiation. Most radio-protective resins are usually prepared with dispersing a metal oxide into the polymer, the metal-containing polymer synthesized by this method exhibits a good absorption to X-ray,[6] but it has poor strength and hardness. Also, the metal oxide is easy to dissipate from the materials, which will pollute the environment. Introducing metal ion to polymer chains[7,8] can mend the shortcoming above mentioned, and improve some physical properties[3,9] of polymer materials.

Styrene (St) is a kind of optical resin that possesses good visible light transparency. In the present paper, we introduced barium ion into the polymer chains of styrene to prepare a series of Ba^{2+}-containing transparent resins. The phase diagram of the transparency of the Ba^{2+}-containing polymer in a three-component system was studied. The Ba^{2+}-containing transparent resins not only exhibit a good radiation shielding properties, but also have a high glass transition temperature and good optical properties, which have practical significance.

Barium dicinnamate ($Ba(CA)_2$) was prepared,[9] the structure might be considered as:



Because $Ba(CA)_2$ was not dissolved in St, methacrylic acid (MA) was chosen to be a cosolvent and a monomer. Thus barium dicinnamate was dissolved in a solution mixture of methacrylic acid and styrene to form a transparent solution. AIBN was added as an initiator. The resulted mixture was pre-polymerized at 57 °C for 20 min, then the content was cast and sealed into a mold consisting of two glass plates and a silicone rubber gasket and was copolymerized in bulk at 57–110 °C for 18 h. The resulted sheets were colorless and transparent with a thickness of 3 mm.

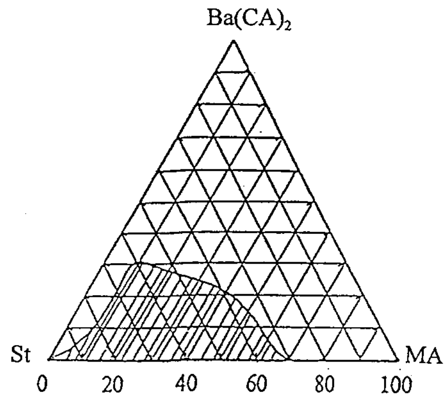


Figure 1. The phase diagram of the polymer transparency of the three-component system $Ba(CA)_2$ / St / MA. (Shadow area is the transparent region.)

The visible light transmittance (at 550 nm) of the sheets was measured. When the transmittance was above 50%, the sheets were recorded as transparent ones; otherwise they were recorded as nontransparent ones. In a phase diagram of the three-component $Ba(CA)_2$ / St / MA was divided into 100 small triangles by the lines that parallel the base and correspond to varying percents of the component (see Figure 1). According to the ratio of every angular vertex, the three components were copolymerized, and the transmittance of the copolymer was recorded. Then, the triangles including the transparent and the nontransparent points were further divided into 25 smaller triangles, and the transmittance at those points was recorded too. Finally, a line was drawn

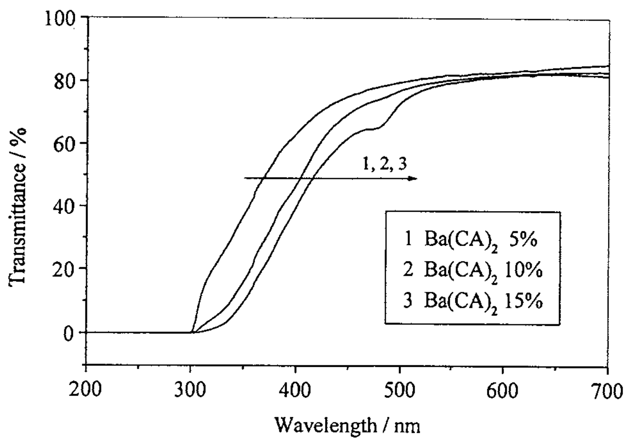


Figure 2. The UV-Visible spectra of the Ba^{2+}-containing optical resins with different $Ba(CA)_2$ content.

between the transparent and nontransparent points, so the phase diagram of the polymer transparency of the three-component system $Ba(CA)_2$ / St / MA was plotted and shown in Figure 1. It indicates that the three-component system has a large transparent phase area of the polymer, the content of $Ba(CA)_2$ could be up to 32 wt%. Therefore we could obtain the optical resins with a high content $Ba(CA)_2$.

The UV–Vis spectra of the three-component copolymer $Ba(CA)_2$ / St / MA were measured (see Figure 2). The visible light transmittance (at wavelength 550 nm) of the polymer was 76–83%, which showed the good transparent properties. The onset wavelength in ultraviolet region was 310 nm, which illustrated that the Ba^{2+}-containing polymers could absorb ultraviolet light partially. This is useful as an optical resin for shielding ultraviolet in a visional field.

The X-ray and γ-ray absorbency of the transparent polymers containing Ba^{2+} for different X-ray and γ-ray energies was measured (see Table 2). Even if the content of $Ba(CA)_2$ was low (5 wt%), the X-ray absorbency of the Ba^{2+}-containing optical polymers was up to a higher value (99.2%). And with increasing $Ba(CA)_2$ content, the optical resins almost could absorb X-ray completely. It indicates that the optical resins containing Ba^{2+} have good absorption to X-ray. In addition, the Ba^{2+}-containing optical resins could absorb γ-ray partially, and with increasing $Ba(CA)_2$ content, the γ-ray absorbency of this kind of transparent polymer was increased. When the γ-ray energies were increased, the γ-ray absorbency of Ba^{2+}-containing optical resins was decreased.

Table 1 The physical properties of Ba^{2+}-containing optical resins[a]

$Ba(CA)_2$ /St /MA /wt%	Trans.[b] /%	T_g[c] /°C	TGA[d] /°C
0 / 88 / 9	89.4	108.6	320.1
5 / 83 / 9	82.1	132.5	323.7
10 / 75 / 13	80.6	141.6	355.1
15 / 65 / 18	79.6	149.3	374.3
20 / 53 / 24	79.5	----	385.4
25 / 43 / 29	76.4	---	---

[a]The sample sheets were of the thickness about 3 mm. [b]Transmittance was the visible light transmittance at wavelength 550 nm. [c]Tg was the glass transition temperature by DSC, at a heating rate of 10 °C/min. [d]TGA was the decomposition temperature of the polymer, the weight loss at which was 5% in nitrogen.

The glass-transition temperatures (Tg) and the decomposition temperatures (TG) of the transparent resins with different $Ba(CA)_2$ contents are shown in Table 1. The results indicate that the glass transition temperatures and the decomposition temperatures of the copolymer were all obviously improved with the $Ba(CA)_2$ content increasing from 0 to 20 wt%. We think there are three reasons, firstly, $Ba(CA)_2$ with two double bonds (C=C) could be acted as a cross-linker. Tg of the copolymer will be higher as cross-linkage increases. Secondly, owing to the strong attraction of the metal ion-bonds in the polymer chains, the motion of chains is limited. The molecular mobility and flexibility are reduced. Thirdly, the carboxyl group in MA unit participated in the interaction to Ba ion, which increased the interaction of the molecular chains. Therefore, the Ba^{2+}-containing optical resins have higher glass-transition temperatures and decomposition temperatures. Introducing Ba^{2+} into optical polymers could obviously improve the heat resistance of the copolymer and make the transparent resins exhibit good thermal properties.

Table 2. The radio-protective properties of Ba^{2+}-containing transparent resins[a]

$Ba(CA)_2$ /wt%	X-ray Absorbency[b] /%	γ-ray Absorbency for different energies[c] /%		
		$E\gamma_1$	$E\gamma_2$	$E\gamma_3$
0	73.1	4.4	4.1	2.3
5	99.2	7.0	5.1	4.0
10	99.8	7.4	6.7	4.2
15	100	8.8	7.6	4.8
20	99.9	8.8	8.3	2.7
25	100	11.1	7.8	4.0

[a]The sample sheets were of the thickness about 3 mm. [b]The X-ray Absorbency was for X-ray energy E_X=8.04 KeV. [c]The γ-ray Absorbency was for different γ-ray energies which were $E\gamma_1$=123 KeV, $E\gamma_2$=344 KeV, $E\gamma_3$=873 KeV, respectively.

The physical properties of the Ba^{2+}-containing optical resins, such as the transparency and the thermal properties, almost did not have changes after irradiation of X-ray and γ-ray for 1 h.

References and Notes

1 M. Olshavsky and H. R. Allcock, *Macromolecules*, **30**, 4179, (1997).

2 T. Matsuda, Y. Funae, M. Yoshida, T. Yamamoto, and T. Takaya, *J. Appl. Polym. Sci.*, **65**, 2247, (1997).

3 S. Eguchi, T. Koyama, H. Asano, and M. Wajima, *Photology*, **15,** 50, (1986).

4 W. Y. Xu, J. R. Cui, Y. S. Wang, and Z. H. Pei, *Chin. J. Polym. Sci.*, **8**, 93, (1990)

5 H. F. Mark, "Encyclopedia of Polymer Science and Engineering," John Wiley & Sons Inc., London (1985), 8, p. 393.

6 M. G. Raspopov, N. V. Levchenko, V. P. Balykin, V. T. Neumerzhitskii, *Tsu. Metallurgiya*, **1985**, 43; *Chem. Abstr.*, **104**, 140872 (1986).

7 E. Iwabori, Japan Patent 60,157,092 (1985); *Chem. Abstr.*, **103**, 202543 (1985).

8 Y. Kaneko, Ch. Shimizu, Y. Hoshino, Y. Harada, Y. Fujita, and H. Okuda, Japan Patent 61 98,765, (1986); *Chem. Abstr.*, **105**, 154497 (1986).

9 Ch. X. Jia, B. Yang, D. H. Lin, Y. J. Li, and J. C. Shen, *Acta Polym. Sinica*, **3**, 316, (1993).