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Polymer 41 (2000) 8305–8309

polymer

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Synthesis, characterization and property studies of Pb^{2+}-containing optical resins

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Received 22 October 1999; received in revised form 15 March 2000; accepted 21 March 2000

Abstract

Lead dimethacrylate ($Pb(MA)_2$) was synthesized and copolymerized with styrene and methacrylic acid, and optical resins containing the heavy-metal ion, Pb^{2+}, were obtained. The monomer-solubility phase diagrams and polymer-transparency phase diagrams were determined and discussed in detail. This series of metal-containing resins possessed good visible light transparency, high refractive index, and good thermal stability. The relationship between the refractive index (n_D), Abbe number (ν_D), heat resistance, radiation shielding properties, and the content of metal salts in optical resins were investigated. The results indicated that adding of metal Pb^{2+} into the optical resins not only exhibited high absorption for X-ray with good visible light transparency, but could also improve the glass transition temperature and refractive index of polymer materials. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Optical resins; Pb^{2+}-containing resins; Properties

1. Introduction

As a result of their excellent properties such as lightness, good transparency, impact resistance, processability, and dyeability, transparent resins are able to extend their application as optical materials replacing inorganic optical materials in various fields[1,2]. Addition of heavy-metal ion into polymer chains, can not only improve the glass transition temperature and refractive index of these materials[3–5], but they can also be used to synthesize functional materials which have radio-resistance properties [6,7] or nonlinear optical properties [8,9]. With the extensive usage of various radiations, there was much interest in the preparation of radio-protective material, especially in the study of transparent radio-protective polymers [3,4,10]. The metals, which could play a role in absorbing radiation, are Ti, Pb, Al, Cr, Mg, Ba, Fe, etc. Lead (Pb) is usually used.

Metal oxide can be regarded as a filler to disperse into the polymer. By this method, the metal-containing polymer exhibited good absorption for X- and γ-rays, but it had poor strength and hardness [11]. In addition, metal oxide was easy to dissipate from materials; which would pollute the environment. If the metal was composited to a component that has reaction activity, and as a monomer when added into the reaction system to synthesize copolymerized resins, the above shortcoming could be overcome. To our knowledge, the synthesis, characterization and property studies of this kind of transparent material, which was prepared by copolymerization with a metal-containing monomer and styrene, have not yet been reported. In this paper, heavy-metal ion Pb^{2+} was introduced as its methacrylate in the reaction. It was regarded as a monomer and copolymerized with styrene and methacrylic acid. Thus a kind of transparent polymer containing Pb^{2+} was successfully synthesized. In addition, the monomer-solubility phase diagrams and polymer-transparency phase diagrams of the system were studied in detail. The optical, physical and radiation-shielding properties were also discussed at different contents of monomer.

2. Experimental

2.1. Materials

Styrene and methacrylic acid were chemical grade and distilled in vacuum before they were used. Lead oxide, 2,2′-azo-bis-isobutyronitrile (AIBN), methanol, ethanol, and other reagents were of analytical grade.

Lead dimethacrylate ($Pb(MA)_2$) was prepared by the

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PII: S0032-3861(00)00212-3

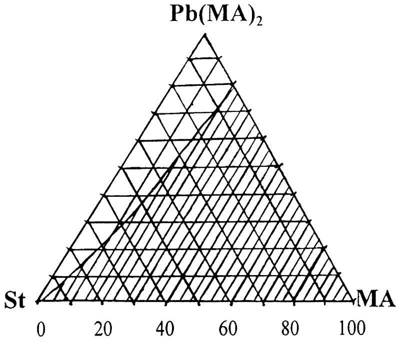

Fig. 1. The monomer-solubility phase diagram of the $Pb(MA)_2$/St/MA three-component system at 60°C (the shaded part is the dissolved region).

procedure as described in Ref. [12]. The structure might be considered as:

$Pb(MA)_2$:CH_2=C(CH_3)–COO–Pb–OOC–C(CH_3)=CH_2

2.2. Synthesis of metal-containing optical resins

$Pb(MA)_2$ was dissolved in a solution mixture of methacrylic acid (MA) and styrene (St) to form a transparent solution. Then AIBN was added as an initiator. The resulting mixture was pre-polymerized at 57°C for 20 min. The content was cast and sealed into a mold consisting of two glass plates and a silicone rubber gasket and was maintained at 52°C for 12 h, 60°C for 4 h, and 70°C for 4 h. Later, it was gradually heated to 100°C at a rate of 5°C/min and was maintained at 100°C for further 3 h to complete the polymerization. The resulting sheets were colorless and transparent with a thickness of 3 mm.

2.3. Phase diagram

$Pb(MA)_2$, MA and St were mixed and the solubility was recorded. In a $Pb(MA)_2$/St/MA three-component phase diagram, a line was drawn between the dissolved and undissolved points, so the monomer-solubility phase diagram of $Pb(MA)_2$/St/MA three-component system was obtained.

After the copolymerization was finished, the visible light transmittance of the sheets was measured. When the transmittance was up to 50%, the sheets were recorded to be transparent. Otherwise, the sheets were not transparent. The polymer-transparency phase diagram was plotted in the same way.

2.4. Measurements

2.4.1. Refractive index and Abbe number

The refractive index (n_D) of Pb^{2+}-containing transparent polymer was measured using an Abbe's refractometer at 23°C. The Abbe number (ν_D) was calculated using the following formula:

$$\nu_D = (n_D - 1)/(n_F - n_C) \qquad (1)$$

where n_D, n_F, and n_C, are the refractive indices at $\lambda = 589.3$, 486.1, and 656.3 nm, respectively.

2.4.2. UV–Vis transmittance

UV–Vis spectra were obtained using a Shimadzu 3100 UV–Vis–near-infrared recording spectrophotometer. Visible light transmittance was recorded at a wavelength of 550 nm.

2.4.3. Thermal properties

The glass transition temperature (T_g) was measured with a Du Pont 910 differential scanning calorimeter (DSC). The measurements were carried out at a heating rate of 10°C/min and were determined over the range of 40–230°C.

The polymer decomposition temperatures were measured by thermogravimetry analysis (TGA) with a Perkin–Elmer TGA-7 thermogravimetric analyzer. The TGA measurements are conducted with a heating rate of 10°C/min in nitrogen. The temperature at which 5 wt% loss was observed is regarded as the polymer decomposition temperature.

2.4.4. Impact resistance

Impact energy was evaluated using an XJ-40A Impact Testing Machine at room temperature, and the impact strength was calculated. The test sheet had no notch.

2.4.5. Surface hardness

Surface hardness was evaluated by pencil hardness.

2.4.6. Radio resistance

The X-ray absorbance of the metal-containing polymers for $E_X = 8.04$ keV was measured by a Si (Li) detector, the X-rays were generated by ^{238}Pu bombardment on Cu- and Pb-targets. The attenuation of X-rays was measured by counts since the intensity of X-rays is in linear proportion to counts.

3. Results and discussion

3.1. Phase diagram

$Pb(MA)_2$ was added into a solution mixture of St and MA. The monomer-solubility phase diagram of $Pb(MA)_2$/St/MA three-component system is shown in Fig. 1. It indicated that there was a wide area where the three components could dissolve each other. St and MA were soluble with each other at all ratios. $Pb(MA)_2$ almost could not be dissolved in St. But in $Pb(MA)_2$/MA two-component system, 20 wt% MA could dissolve 80 wt% $Pb(MA)_2$ at 60°C, which indicated that the solubility of $Pb(MA)_2$ in MA was very good, and it could be further improved when the temperature is increased. From Fig. 1, it can be seen that only when MA content is low and $Pb(MA)_2$ content is high, the three monomers could not dissolve each other. In the solution

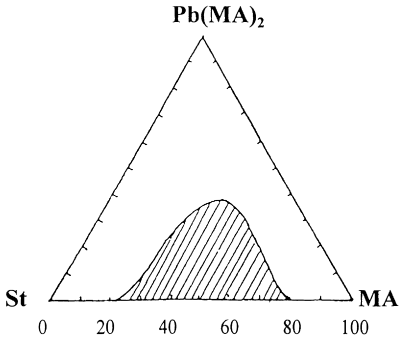

Fig. 2. The polymer-transparency phase diagram of the Pb(MA)$_2$/St/MA three-component copolymerization system (the shaded part is the transparent region).

mixture of St and MA, the solubility of Pb(MA)$_2$ increased almost linearly with the increasing content of MA.

AIBN was added into the Pb(MA)$_2$/St/MA solution mixture, and the polymerization was completed. As a result, the copolymerization resin samples were obtained, and the transparency was recorded. The polymer-transparency phase diagram of the Pb(MA)$_2$/St/MA copolymerization system is shown in Fig. 2.

From the comparison with Fig. 1, it should be noted that the transparent area of the copolymer was smaller than the solubility area of the monomer in the Pb(MA)$_2$/St/MA system. From Fig. 2, it can be seen that when the ratio of St was lower (below 20 wt%) or the ratio of MA was lower (below 23 wt%), the copolymerization reaction led to phase separation and the three-component copolymers were not transparent. However, when the contents of MA and St were similar, the copolymerization resins were transparent. We suggest that St might play a role in regulating the compatibility of MA and Pb(MA)$_2$. When the ratio of St was lower, and due to the high homopolymerization reaction activity of Pb(MA)$_2$ and MA, there were many homopolymers with different refractive indices ($\Delta n_D > 0.009$) in the Pb(MA)$_2$/St/MA three-component copolymers. As a result, the polymer was not transparent. On the other hand, when the ratio of MA was lower, the Pb(MA)$_2$ monomer could be dissolved in the system. During the process of copolymerization, however, the polymer chain of Pb(MA)$_2$ could not be dissolved and it was precipitated from the copolymerization system, and hence the resulting resins in this area were not transparent.

From Fig. 2, it is worth mentioning that there was a large polymer-transparent area when the ratio of monomer was fit. The content of Pb(MA)$_2$ could be up to 40 wt%, therefore we could obtain the optical resins with a high content of Pb(MA)$_2$.

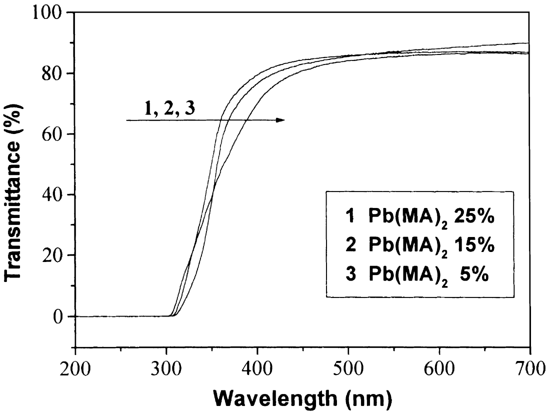

Fig. 3. The UV–Vis spectra of Pb^{2+}-containing optical resins with different Pb(MA)$_2$ content.

3.2. Relationship between the ratio of monomer and the transparency of the polymer

The UV–Vis spectra of the Pb(MA)$_2$/St/MA three-component copolymer were measured and are shown in Fig. 3. The visible light transmittance (at wavelength 550 nm) of the polymers was 80–88%, which showed the good transparent properties. The onset wavelength in UV was 320 nm, which indicated that the Pb^{2+}-containing polymers could absorb a part of UV light. This property helps in its use as an optical resin for shielding UV light in a visional field.

In a visible light transparent region, the mole ratio of MA to Pb(MA)$_2$ ($K = M_{MA}/M_{Pb(MA)_2}$) had an important effect on the transparency of the resins. When K value was in the range from 4.7 to 8.0, the copolymer was transparent, and beyond this range it was not transparent. In addition, it should be noted that when the value of K was between 4.7 and 6.2, the copolymerization system became semitransparent or opaque at the beginning period of the copolymerization reaction, and then gradually became transparent as the polymerization proceeded. However, the transparent property of the final copolymers was not good and uniform. When K was about 7.2, the copolymerization system was transparent during the whole process of copolymerization reaction, and the final copolymers were optically uniform. Therefore, with suitable ratio of contents, we could obtain the optical resins with a high content of Pb(MA)$_2$ and good transparent properties.

3.3. The relationship between optical property and the content of MA

The relationship between refractive index, Abbe number and MA contents in the Pb(MA)$_2$/St/MA system is shown in Fig. 4. The content of Pb(MA)$_2$ was fixed at 10 wt%. As the content of MA increases, n_D of the copolymer decreases linearly, but ν_D increases linearly. In fact, the refractive index of copolymer was the sum of the contribution of each monomer component that was proportional to its content. By the theory of 'sum', according to the n_D value of polystyrene ($n_{PS} = 1.590$), we could calculate the refractive index of the homopolymer of Pb(MA)$_2$ and MA. and the values are $n_{P(Pb(MA)_2)} = 1.630$ and $n_{PMA} = 1.499$, respectively.

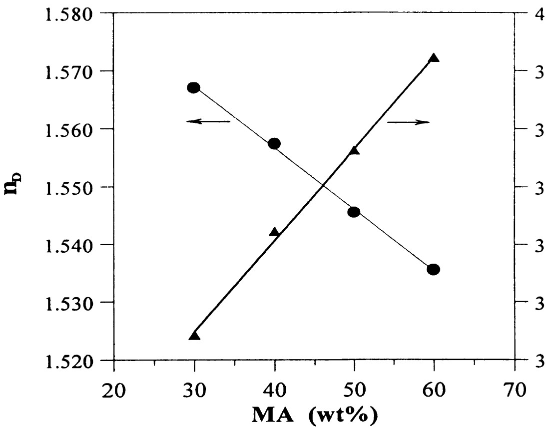

Fig. 4. The relationship between the refractive index of Pb^{2+}-containing optical resins and the MA content ($Pb(MA)_2$ content 10 wt%).

3.4. The relationship between optical property and the content of metal salts

In the $Pb(MA)_2$/St/MA system, as the $Pb(MA)_2$ content was varied, the refractive index and Abbe number were changed accordingly (see Fig. 5). When the content of MA was fixed at 40 wt%, with the content of $Pb(MA)_2$ increasing from 0 to 30 wt%, the refractive index (n_D) increases gradually and linearly from 1.554 to 1.563, and the Abbe number also increases gradually and linearly. This result in which n_D and ν_D increase at the same time was different from that of most other materials. Similar conclusions are reported in Ref. [6]. From the theory of the sum of refractive index, we calculated the refractive index of the homopolymer of $Pb(MA)_2$ and MA. The values were $n_{P(Pb(MA)_2)} = 1.622$, $n_{PMA} = 1.501$, which are similar to the above results. Therefore, the average results were $n_{P(Pb(MA)_2)} = 1.626$, $n_{PMA} = 1.500$. The conclusion indicated that the refractive index of $Pb(MA)_2$ was higher than that of other monomers. So the addition of $Pb(MA)_2$ into the copolymerization system could improve the refractive index of optical resins.

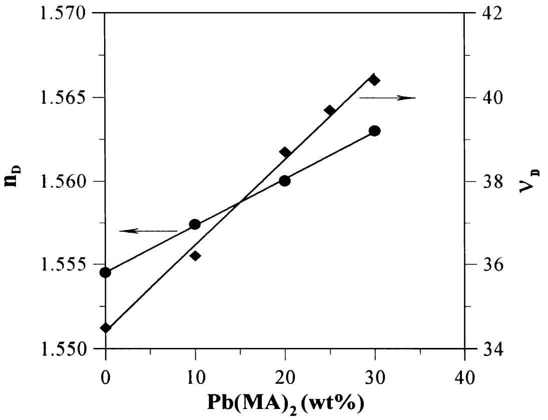

Fig. 5. The relationship between the refractive index of Pb^{2+}-containing optical resins and the $Pb(MA)_2$ content (MA content 40 wt%).

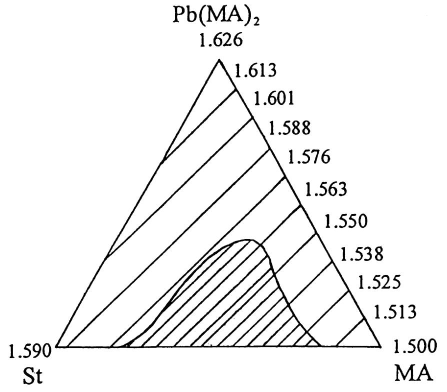

Fig. 6. The polymer-transparency phase diagram of the $Pb(MA)_2$/St/MA three-component copolymerization system with the same refractive index line (the shaded part is the transparent region).

From the refractive index (n_D) values of the homopolymer of $Pb(MA)_2$, MA, and St, n_D value of the copolymer of $Pb(MA)_2$/St/MA system was calculated. The polymer-transparency phase diagram with the same n_D value line is shown in Fig. 6. It could be seen that in the transparent area of the $Pb(MA)_2$/St/MA system, the n_D values of the copolymer changed from 1.518 to 1.574. From the figure, the n_D values of the copolymer with different contents could also be obtained.

Due to the lower refractive index of MA, the n_D values of copolymer were obviously decreased. In order to improve the n_D value of the copolymer, decreasing the MA ratio and increasing the $Pb(MA)_2$ or St ratio was found to be effective. So, adding the Pb^{2+} metal ion into an optical polymerization system could result in transparent resins with a high refractive index.

3.5. The heat resistance of metal-containing optical resins

The glass transition temperatures (T_g) and the polymer decomposition temperatures (T_G) of optical resins with different $Pb(MA)_2$ contents are shown in Table 1. The results indicated that T_g improved when the $Pb(MA)_2$ content increased from 5 to 20 wt%. We thought that $Pb(MA)_2$ containing two double bonds (C=C) could act as a cross-linker. Cross-linkage increased as the $Pb(MA)_2$ content increased. Owing to the strong attraction of the metal ion-bond in the polymer chains, the movement of the chains was limited. The molecular mobility and flexibility were reduced. Therefore, the optical resins containing metals had a higher glass transition temperature. Addition of Pb^{2+} metal ion into optical polymers could improve the glass transition temperature.

The polymer decomposition temperatures (T_G) of optical resins were measured by TGA. The results indicated that the decomposition temperatures of optical resins were improved drastically with increasing $Pb(MA)_2$ content. Thus, the Pb^{2+}-containing optical resins exhibited good thermal stability.

Table 1
The physical properties of Pb^{2+}-containing optical resins

$Pb(MA)_2$ (wt%)	Trans. (%)[a]	Density (g/cm^3)	Surface hardness	Impact strength (kgf cm/cm^2)	T_g (°C)[b]	T_{G}A (°C)[c]	X-ray absorbance (%)[d]
0	89.4	1.116	H	5.3	108.6	320.1	73.1
5	85.1	1.165	2H	10.4	126.4	352.7	97.2
10	80.6	1.217	2H	6.7	132	335.1	99.7
15	86.6	1.269	3H	6.99	151.3	368.5	99.8
20	83.2	1.329	3H	5.45	148	380.6	99.9
25	87.1	1.378	3H	1.74	–	–	100

[a] Visible light transmittance at wavelength 550 nm.
[b] The glass transition temperature obtained by DSC.
[c] The polymer decomposition temperature, 5% by weight loss in nitrogen.
[d] The X-ray absorbance for energy $E_X = 8.04$ keV.

3.6. Mechanical properties of Pb^{2+}-containing optical resins

The physical properties of Pb^{2+}-containing optical resins are shown in Table 1.

Impact strength: The Pb^{2+}-containing optical resins showed better impact strength than PS. But as more Pb^{2+} ions were dispersed in the polymer, owing to the strong attraction of the ionic bond, the rigidity of the molecular chain increased sharply, and the movement of molecular chain came up against more resistance. As a result, the impact strength of metal-containing optical resins decreased with increasing $Pb(MA)_2$ contents.

Surface hardness: The surface hardness of Pb^{2+}-containing optical resins was measured as 2H–3H. Because of their high degree of cross-linking and high rigidity of the molecular chain containing metal ion bond, the surface hardness of Pb^{2+}-containing optical resins was obviously improved compared to that of pure PS (HB).

Density: With increasing $Pb(MA)_2$ content, the density of optical resins increases linearly. This was because the density of metal salts was higher than that of other monomers.

3.7. Radio resistance

The X-ray absorbance of optical polymers containing Pb^{2+} for $E_X = 8.04$ keV was measured and is shown in Table 1. Even if the content of $Pb(MA)_2$ was low (5 wt%), the X-ray absorbance of optical polymers containing Pb^{2+} was high (97.2%). With increasing $Pb(MA)_2$ content, the optical resins could absorb almost all the X-rays. It is evident that the optical resins containing Pb^{2+} had good absorption for X-ray.

4. Conclusions

Lead dimethacrylate ($Pb(MA)_2$) was copolymerized with styrene and methacrylic acid. The optical resins containing heavy-metal ion Pb^{2+} were successfully synthesized. There was a wide monomer-dissolved phase region and a large copolymer-transparent phase area for the $Pb(MA)_2$/St/MA three-component copolymerization system. In the transparent area of the copolymer, the $Pb(MA)_2$ content could be up to 40 wt%. The Pb^{2+}-containing optical resins showed good transparency in the visible light region. The refractive index of the homopolymer of $Pb(MA)_2$ and MA were calculated, which were $n_{\mathrm{P(Pb(MA)_2)}} = 1.626$, $n_{\mathrm{PMA}} = 1.500$. Addition of Pb^{2+} metal ion into the optical resins not only exhibited high absorption for X-ray with good visible light transparency, but also could improve the glass transition temperature and refractive index of polymer materials.

Acknowledgements

This work was supported by National Science Fund for Distinguished Young Scholars of China (No. 29925412) and the Trans-Century Program of Talents, Ministry of Education, People's Republic of China.

References

[1] Olshavsky M, Allcock HR. Macromolecules 1997;30:4179–83.
[2] Matsuda T, Funae Y, Yoshida M, Yamamoto T, Takaya T. J Appl Polym Sci 1997;65:2247–55.
[3] Eguchi Sh, Koyama T, Asano H, Wajima M. Photology 1986;15:50–5.
[4] Xu WY, Cui JR, Wang YSh, Pei ZHH. Chin J Polym Sci 1990;8:93–6.
[5] Jia ChX, Yang B, Lin DH, Li YJ, Shen JC. Acta Polym Sinica 1993;3:316–21.
[6] Jpn Kokai Tokkyo Koho, 157092, 1985.
[7] Jpn Kokai Tokkyo Koho, 98765, 1986.
[8] Stucky GD, MacDougall JE. Science 1990;247:669–76.
[9] Gao MY, Yang Y, Yang B, Bian FL, Shen JC. J Chem Soc Faraday Trans 1995;91:4121–5.
[10] Mark HF. Encyclopedia of polymer science and engineering, vol. 8. New York: Wiley, 1985 (p. 393).
[11] European Patent appl. 19121
[12] Dave AM. Polymer 1984;25:1020–2.