

Study on Syntheses and Properties of 2,2'-Mercaptoethylsulfide Dimethacrylate Transparent Homo- and Copolymer Resins Having High Refractive Index

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Received 24 January 1999; accepted 21 July 1999

ABSTRACT: 2,2'-Mercaptoethylsulfide dimethacrylate (MESDMA) was synthesized from 2,2'-mercaptoethylsulfide (MES) by a Phase-Transfer Catalysis technique and, was characterized and corroborated by ¹H-NMR and FTIR spectra. Except for the poor impact strength, the MESDMA homopolymer resin shows better comprehensive properties, such as a higher refractive index (1.625), lower dispersion (Abbe's number 36), and good heat-resistance (T_g 150°C) and surface hardness (3H), etc. Copolymerizing with styrene (St) can modify most of the properties of the resin. The refractive index, Abbe's number, onset wavelength, density, water-absorption ratio, and absorption intensity of peaks in NIR region, etc. all display a regular change along with the proportion of MESDMA/St. The main absorption peaks in NIR region are assigned as follows: 1680 nm (first overtone) and 1144 nm (second overtone) to the phenyl C—H vibration of polystyrene; 1694 nm (first overtone) to $\nu(\text{CH}_3)$; 1730 and 1750 nm (first overtone) to $\nu(\text{CH}_2)$ for ordinary CH_2 and for CH_2 connected with S or COS groups, respectively; and 1186 nm (second overtone) to aliphatic C—H vibration. The prominent advantage achieved by copolymerization is that the impact strength can be improved as much as 10-fold at a proper composition of the monomers (75% St). © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1474–1479, 2000

Key words: 2,2'-mercaptoethylsulfide dimethacrylate; phase-transfer catalysis; transparent resin; sulfur-containing resin; copolymerization

INTRODUCTION

Since plastics are lightweight, fragmentation-resistant, and easy to be dyed in comparison with glasses, they have been developed rapidly in recent years for application as optical elements such as for lenses of eyeglasses and cameras.¹

However, the refractive index of the currently widely employed resins [poly(ethylene glycol bis-allylcarbonate), CR-39] is 1.50 or less and small.¹ Generally, plastic materials for optical products are strongly required to exhibit high refractive index and low dispersion (with less chromatic aberration). To achieve this aim, sulfur element and halogen element (except for fluorine), especially the former, must be used in the polymer structure design.² Resins containing sulfur have the properties of high refractive index, low dispersion, and lightweightness, the heat stability is especially better than that of resins containing halogen.

Correspondence to: C. Gao.

Contract grant sponsor: Natural Science Foundation of China; contract grant number: 59803006.

Contract grant sponsor: National Education Ministry of China.

Journal of Applied Polymer Science, Vol. 75, 1474–1479 (2000)
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The most convenient and effective way to prepare such a kind of resin is to combine mercapto-containing compounds with double bond-bearing compounds to obtain monomers and then to polymerize by radical initiation. The important methods to synthesize such kinds of monomers from thiols include (1) dehydrogen halide between thiol and halogen substituted alkene (e.g., *p*-chloromethylstyrene) to form sulfide linkage³; (2) addition reaction between thiol and alkenyl isocyanate (e.g., *p*-vinylphenylisocyanate) to form thiourethane linkage⁴; and (3) dehydrogen oxide between thiol and unsaturated carboxylic acid (e.g., methacrylic acid) or dehydrogen chloride between thiol and unsaturated carboxyl halide (e.g., methacryl chloride, MC) to form thioester linkage.⁵ The third way is more acceptable because of the better solubility (usually liquid) and polymerizability of the monomers. The acidity of thiol is stronger than that of alcohol, so the esterification of thiol with carboxylic acid is more difficult, and even if the monomer could be synthesized, the color is usually poor and it is not easy to control the double bonds during the polymerization. Phase transfer catalysis (PTC) has been widely used in nucleophilic substitution, oxidation, and dichlorocarbene, etc., and it can also be used to esterify thiol to obtain a monomer with excellent properties.⁶

In this paper, 2,2'-mercaptoethyl sulfide dimethacrylate (MESDMA) was synthesized from 2,2'-mercaptoethyl sulfide (MES) and MC by a PTC reaction at low temperature (<10°C), and the homo- and copolymer (with styrene) resins made from MESDMA were prepared by casting the monomer mixture in glass molds with gaskets. The resins so obtained are colorless and transparent, and some basic properties of the MESDMA homopolymer and MESDMA/St copolymer resins were characterized.

EXPERIMENTAL

Materials

MC, prepared from methacrylic acid and SOCl₂ in the presence of LiCl, was purified through distillation for three times, bp: 95–99°C, $n_d^{20} = 1.4458$. Triethylbenzyl-ammonium chloride (TEBA) was prepared from triethylamine and benzyl chloride in 1,2-dichloroethane and was recrystallized in 1,2-dichloroethane/anhydrous ethanol. Thiodigly-

col (TDG), C.P., and all other A.R. reagents and solvents were used as received.

Synthesis of MESDMA by PTC Reaction

MES was synthesized through a hydrochloride/thiourea method referenced to literature.⁷ The crude product was purified by distillation in reduced pressure (bp: 120–121°C/0.66 kPa). The final product is colorless liquid; yield 82.5%, $n_d^{20} = 1.5900$, Abbe's number (ν_d , which proportions inversely with chromatic aberration, higher ν_d means lower light dispersion) is 36.5. In a three-necked 1000-mL round-bottomed flask equipped with a mechanical stirrer, a thermometer, and a dropping funnel, 50 g (0.324 mol) MES, 250 mL dichloromethane, 7.5 g TEBA, and cooled KOH solution (50 g KOH in 500 mL distilled water) were introduced. While violently stirring and maintaining the temperature at 5–7°C with ice/water bath, 65 mL MC (0.68 mol) in 100 mL dichloromethane was dropped into the above solution for 0.5 h. White fog appeared in this stage. After continuously stirring at 1.5°C for 2 h, the dichloromethane layer was separated out and washed with dilute HCl and 10% NaHCO₃ successively, then washed with distilled water until neutral. Finally, the solution was dried with CaCl₂, the solvent evolved, and the solution filtered to obtain the monomer, which is a colorless and transparent liquid; yield 88.9%, $n_d^{20} = 1.5755$, $\nu_d = 32.4$.

MESDMA, whose chemical structure is



was characterized and corroborated by FTIR and ¹H-NMR. FTIR, MES: 3300 cm⁻¹ (OH) disappeared, 2546 cm⁻¹ (SH) appeared; MESDMA: 2546 cm⁻¹ (SH) disappeared, 1663 cm⁻¹ (unsaturated COS), 1629 cm⁻¹ (C=C), and 3090 cm⁻¹ (=CH₂) appeared. ¹H-NMR, MES: 1.73 (t, J = 1.6, SH), 2.6–2.8 (m, SCH₂); MESDMA: 1.97 (s, CH₃), 5.60 and 6.07 (s, =CH₂), 3.07 (COSCH₂), 2.82 (SCH₂).

Preparation of Transparent Resins

Monomers and 0.3% (by monomers' weight) AIBN and mold release agent were mixed together, degassed, and prepolymerized at 60°C until all the solids dissolved. The mixture was cooled and de-

gassed until no bubbles evolved, then poured into glass mold and the mold was heated and cured in an oven at 5°C/0.5 h to 100°C, which was maintained for 2 h, and the oven was then turned off. When the temperature was decreased to 30°C, the mold was unloaded to obtain a transparent resin 3 ± 0.2 mm thick.

Characterization

The analysis instruments and conditions are as follows: Bruker IFS66V FTIR spectrometer, using a NaCl plate and measured at reduced pressure; Varian FT-80A NMR spectrometer, CDCl₃ as solvent; Shimadzu UV3100 UV-vis-NIR spectrometer, air as reference; W2S-1 refractometer, α -bromonaphthalene as contact media and measured at a constant 20°C.

RESULTS AND DISCUSSION

MESDMA Homopolymer Resin

The homo- or copolymerizability of MESDMA is very excellent, and the obtained resins are all thermosetting due to the two double bonds in the molecule. The sulfur content is higher in the MESDMA molecule (33.1%); therefore, the refractive index of the MESDMA homopolymer resin is also higher, $n_d^{20} = 1.625$, but the dispersion of the index is still lower, Abbe's number $\nu_d = 36$ ($n_f - n_c = 1736 \times 10^{-5}$). It can be calculated from the Fresnel equation, $r = (n - 1)^2 / (n + 1)^2$, where r is one-side reflectance and n is the refractive index, that the total reflectance on the two sides of the resin is 11%, which means that the highest transmittance is 89%. Figure 1 shows that the transmittance is about 85% in the vis region, so the transparency of the resin is good enough (if ordinary glass molds are substituted by optical glass molds, the transmittance can be improved further). The absorptions at 1750 and 1186 nm are attributed to the first and second overtone bands of the C—H expansion vibration, respectively.⁸ The light below 340 nm is absorbed totally by the 3-mm-thick resin, and it is especially important for eyeglasses to eliminate the harm of UV light to human eyes. The other merits include high surface hardness (pencil hardness $\geq 3H$) and good heat resistance [$T_g = 150^\circ\text{C}$ by DDSC, very small deformation in thermal mechanical analysis (TMA)]. The greatest weakness of the resin, which is of lower strength (Charpy unnotched

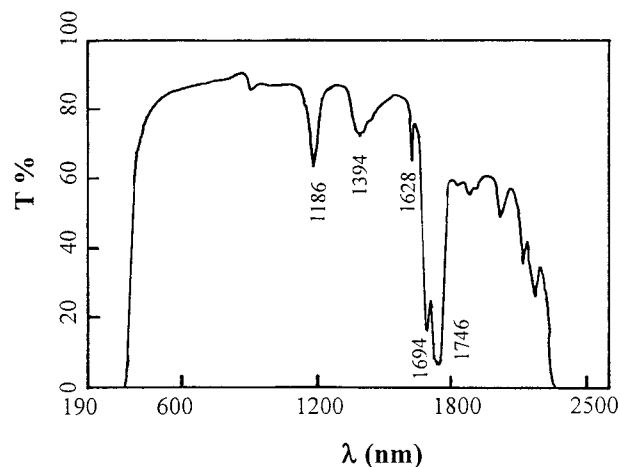


Figure 1 Transmittance spectrum of MESDMA homopolymer (3 mm thick).

impact strength is 0.9 kJ m^{-2}), is caused by the highly crosslinked structure and can be improved through copolymerization with other monoalkenyl monomers, for example, styrene (St).

MESDMA–St Copolymer Resins

Most of the properties of homopolymer resins, such as refractive index, dispersity, and strength, etc., can be adjusted through copolymerization with other monomers to fit the different requirements in different situations, and St is the usually selected monomer in consideration of its good cosolubility and optical properties. The refractive index and Abbe's number are usually contradictory in an ordinary copolymer system, which means that when the refractive index increases with the content the Abbe's number decreases. A great difference is shown in the MESDMA–St copolymer system in that both n_d and ν_d increase lineally with the amount of MESDMA (Fig. 2) because of the higher n_d and ν_d of MESDMA homopolymer than those of polystyrene (PS). The refractive index of the copolymers calculated from either weight ratio of the components or the Lorentz equation, $R = (n^2 - 1)M / [(n^2 + 2)\rho]$, where R is mol refractivity and ρ is the density of the copolymer, are both very close to the measured one (Fig. 2, the dashed line, by weight ratio).² The transparency in the visual region of all the copolymers is perfectly satisfied; the average light transmittance is more than 85%. Along with increasing of MESDMA content, the onset wavelength of the copolymer resins in UV region moves lineally to the longer wavelength (Fig. 3).

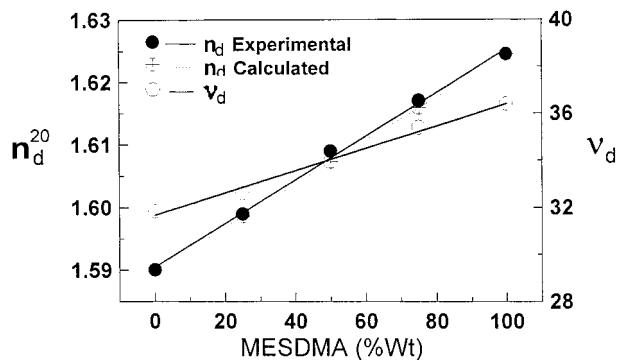


Figure 2 Variation of refractive index (n_d^{20}) and Abbe's number (v_d) of MESDMA–St copolymer resins versus the amount of MESDMA.

This is beneficial to eliminate the injury of UV light to human eyes if it is used as eyeglass material.

The variation of absorption intensity of the MESDMA–St copolymer in the near-infrared region depends closely on the monomer proportion, especially for peaks around 1740, 1680, and 1186, 1144 nm (Figs. 4 and 5). A strong absorption peak assigned to the PS homopolymer appears at 1680 nm. It weakens linearly along with decreasing of the St ratio in the MESDMA–St copolymers, and the peak moved from 1680 to 1694 nm gradually [Fig. 4(a)]. When MESDMA/St = 50/50, the peak becomes the widest and shows clearly that it is overlapped by two peaks. Furthermore, the absorption at 1680 nm shows a good linear relation to the St amount [Fig. 4(b)]. According to these results and also cited by other researchers,⁸ we are sure that the peak at 1680 nm is attributed to

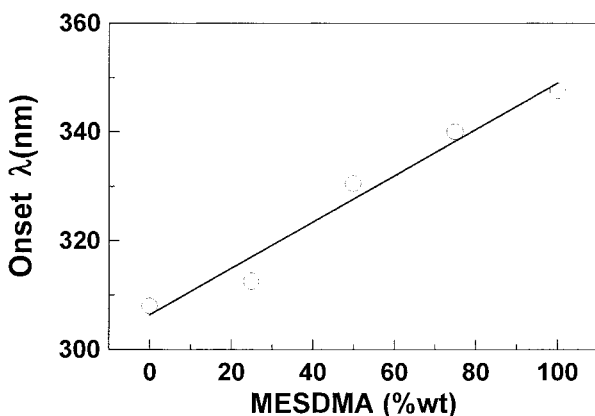


Figure 3 Variation of onset wavelength of MESDMA–St copolymer resins in UV region versus the amount of MESDMA.

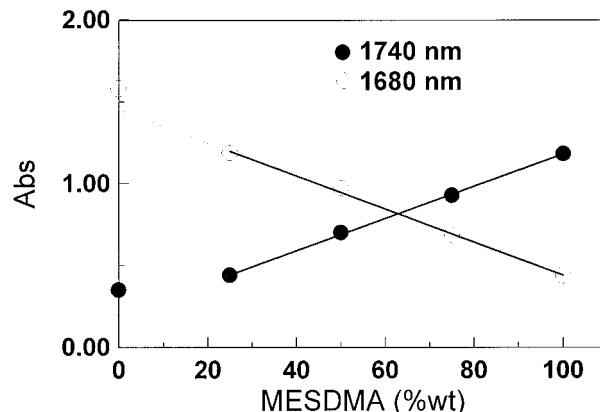
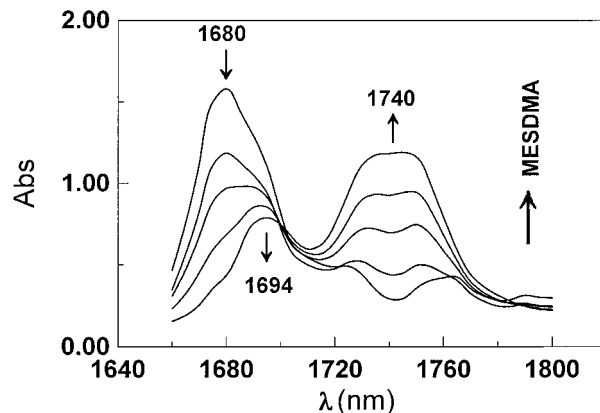


Figure 4 (a) Variation of absorption bands around 1680 and 1740 nm of MESDMA–St copolymer resins versus the amount of MESDMA. (b) Effect of MESDMA amount on the absorption of MESDMA–St copolymer resins at 1680 and 1740 nm.

the first overtone band of the aromatic $\nu(\text{C—H})$ vibration in PS, while the peak at 1694 nm is attributed to the first overtone band of the aliphatic $\nu(\text{CH}_3)$ vibration in the MESDMA homopolymer. The higher absorption of PS in Figure 4(b) [also in Fig. 5(b)] is due to the universal lower transmittance of PS in the whole measured region (170–2500 nm).

It can be seen from Figure 4 that the peak at 1746 nm in the MESDMA homopolymer (Fig. 1) is composed actually of two peaks: 1730 and 1750 nm, and the latter is slightly stronger than is the former. The intensity of the both peaks strengthens with increasing of the MESDMA amount, and the increasing ratio remains almost the same [Fig. 4(a)]. The absorption at the middle point of 1730 and 1750 nm (i.e., 1740 nm) shows a good linear relation with the amount of MESDMA [Fig. 4(b)]. As a result, we are assured that the two peaks are attributed to the first overtone band of

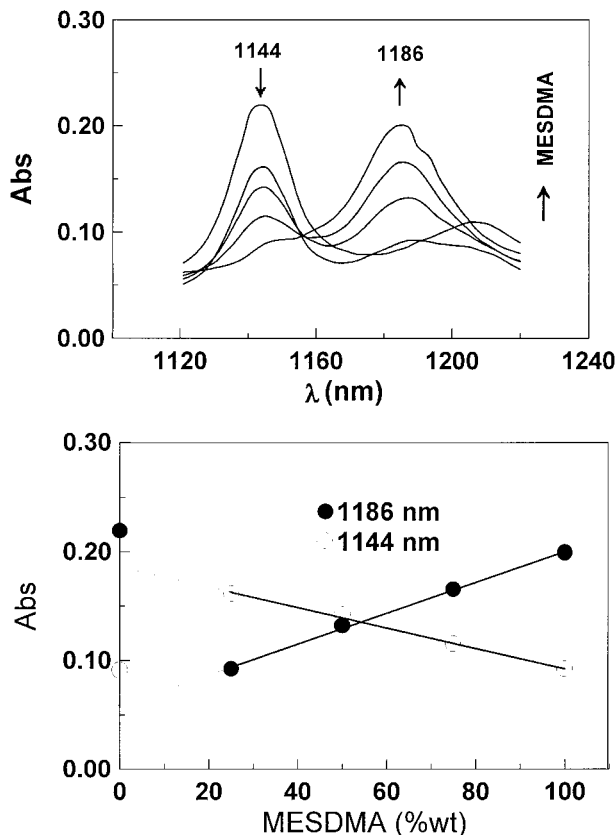


Figure 5 (a) Variation of absorption bands around 1144 and 1186 nm of MESDMA–St copolymer resins versus the amount of MESDMA. (b) Effect of MESDMA amount on the absorption of MESDMA–St copolymer resins at 1144 and 1186 nm.

aliphatic $\nu(\text{CH}_2)$ vibration,⁸ and it means that there are two different kinds of CH_2 groups. In both the spectra of PS and the MESDMA homopolymer, there exists the absorption peak at 1730 nm and the peak shape is similar. But it is different for the peak at 1750 nm; this peak is only in the MESDMA homopolymer, not in the PS homopolymer [Fig. 4(a)]. So, the peak at 1730 nm is assumed to be attributed to the absorption of ordinary CH_2 groups, while the peak at 1750 nm, to the absorption of CH_2 groups connected with S or COS groups.

Figure 5(a) shows that the intensity of the second overtone bands at 1144 nm, which belong to the aromatic C–H vibration, weakens along with increasing of the MESDMA amount in the MESDMA/St copolymers, while that at 1186 nm, which belongs to the aliphatic C–H vibration, strengthens. The absorption at 1144 and 1186 nm fits well linearly, decreasing and increasing along with increasing of the MESDMA ratio [Fig. 5(b)],

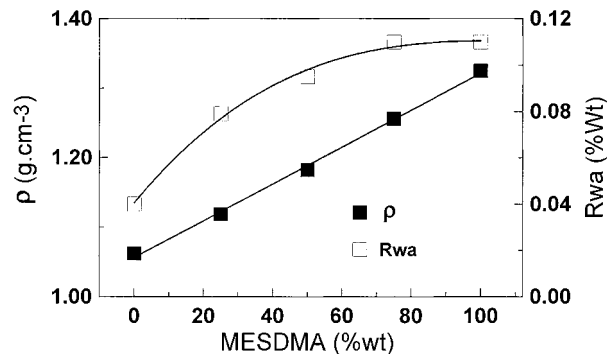


Figure 6 Effect of MESDMA amount on the density (ρ) and water-absorption ratio (R_{wa}) of MESDMA–St copolymer resins.

respectively. For different kinds of aliphatic groups, the peak at 1186 nm can move in the range of several nanometers to a decade nanometer, for example, 1174 nm for PMMA, 1180 nm for poly(2,2,3,3-tetrabromobutane-1,4-diol dimethacrylate), 1186 nm for poly(thiodiglycol dimethacrylate), and 1186–1192 nm for MESDMA-2-methylthiomethyl-1,4-dithiane copolymers.⁹

The density of the copolymer resins shows better linear relation with the monomer compositions (Fig. 6), which is between 1.062 (PS) to 1.325 g cm^{-3} (MESDMA homopolymer). Therefore, these copolymer resins belong to the lightweight type of optical plastics compared with those polymers with the comparable refractive index, which contain halogen elements or heavy metal elements (e.g., Pb, Ba, Cd, La). The water-absorption ratio (R_{wa}) increases slightly with increasing of the MESDMA amount in the copolymer resins (Fig. 6), but it is still 3–4 times lower than that of

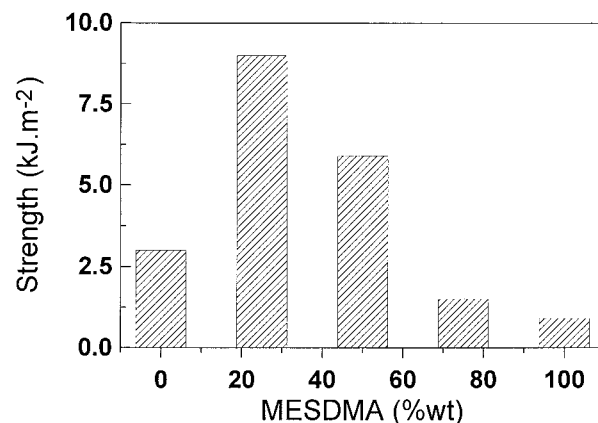


Figure 7 Effect of MESDMA amount on the Charpy impact strength of MESDMA–St copolymer resins.

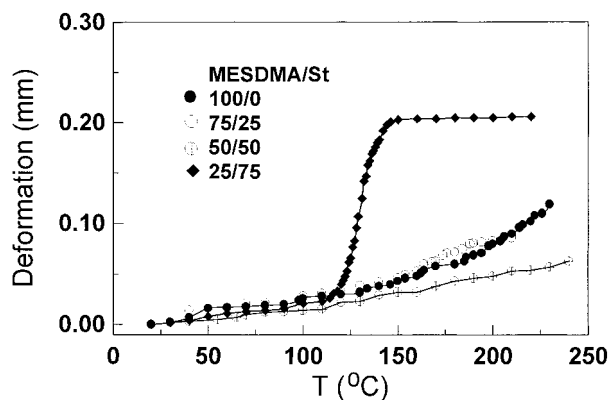


Figure 8 TMA of MESDMA–St copolymer resins.

PMMA in the same measuring condition even if for the largest MESDMA homopolymer.

The strength of MESDMA homopolymer resin can be modified and improved by copolymerizing with St in some special composition (Fig. 7). The largest impact strength (9 kJ m^{-2}) appears at 75% of St (wt), which is 10 times larger than that of the MESDMA homopolymer. Through leading St linkage into the MESDMA homopolymer networks, the distance between the crosslinked point is lengthened and the crosslinked degree is lessened. Consequently, the brittleness of the MESDMA homopolymer is modified and the strength is improved when MESDMA/St is in the proper range. The mechanical property must be considered for the resin to be used in any case, so copolymerization with St is an important way to modify the impact strength to make the resin usable.

The flexibility of the molecular chain is improved by introducing St linkage; as a result, the heat resistance and the surface hardness will be reduced. Figure 8 shows that the deformation

extent in TMA remains smaller when St content is less than 75% and the transition temperature obviously cannot be observed. When the content of St is up to 75% (wt), there is an obvious change of the deformation, by which the T_g can be determined (121°C). The heat-resistance is lowered in comparison with the MESDMA homopolymer (T_g 150°C), but it is still high enough for usual applications, for example, eyeglasses and cameras. Furthermore, the pencil hardness of the copolymer resins remains 1H even if the St content is up to 90%, which, although not bad, should be strengthened further with hard coating.

The authors wish to acknowledge with gratitude the financial support from the Natural Science Foundation of China (59803006) and the National Education Ministry of China.

REFERENCES

1. Kayanoki, H.; Ishizuka, S.; Takigawa, A. Eur. Patent 0 524 477, 1992.
2. Van Krevelen, D. W. *Properties of Polymers*, 3rd ed.; Elsevier: New York, 1990.
3. Yutaka, T.; Fumie, W. Eur. Patent 0 424 144, 1991.
4. Mikito, N.; Yusuke, K.; Hiroshi, F.; Akira, M. Jpn. Patent 04 080 213, 1992.
5. Shingo, M.; Masahiro, A.; Toshihiro, N.; Yasuji, K. Jpn. Patent 03 011 054, 1991.
6. Gao, C. Y.; Yi, X. S.; Yang, B.; Shen, J. C. *ACTA Polym Sin* 1998, 16, 306.
7. Reid, E. E. *Organic Chemistry of Bivalent Sulfur*; Chemical: New York, 1958.
8. Siesler, H. W.; Holl-Moritz, K. *Infrared and Raman Spectroscopy of Polymers*; Marcel Dekker: New York, 1980.
9. Gao, C. Y.; Yang, B.; Shen, J. C. *Chem J Chin Univ* 1998, 19, 1840.