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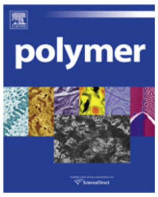

Synthesis and characterization of trifluoromethyl substituted styrene polymers and copolymers with methacrylates: Effects of trifluoromethyl substituent on styrene

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ABSTRACT

2-Trifluoromethyl styrene (2TFMS), 2,5-bis(trifluoromethyl) styrene (25BTFMS), and 3,5-bis(trifluoromethyl) styrene (35BTFMS) were synthesized. These styrenes were readily polymerized in bulk and also in solution using AIBN as a free radical initiator. The polymerization rate of these trifluoromethyl substituted styrenes and other monomers such as styrene (St), pentafluorostyrene (PFS) and 4-trifluoromethyl-tetrafluorostyrene (TFMTFS) were measured in benzene and dioxane by monitoring the ^{1}H NMR spectra of the double bond hydrogen. The order of polymerization rates was TFMTFS > 35BTFMS > 25BTFMS > PFS > 2TFMS > St. T_gs of styrene polymers with CF_3 substituted on the ortho position of the phenyl ring were much higher than those of the meta and para substituted styrenes due to the steric hindrance of the bulky CF_3 group close to the polymer main chain, which resulted in a decrease in the segment mobility of the polymer chains and an increasing T_g of the polymers. The copolymers of 2TFMS with methyl methacrylate (MMA) and also 25BTFMS with trifluoroethyl methacrylate (TFEMA) were prepared. T_gs of the copolymers were in the range of 120–145 °C and the copolymers were transparent and thermally stable. The copolymer films were flexible and exhibited high transmittance as the homopolymers of MMA and TFEMA. Thus, these copolymers may be utilized as novel optical materials.

1. Introduction

Polystyrene (PS) is a commercially important polymer with good light transmittance. The favorable physical properties of PS coupled with ease of processing make it useful as optical device materials [1]. However, high losses in the visible and near infrared region are dominated by the combinations of stretch and deformation vibrations of C–H bonds [2,3]. When heavier atoms such as deuterium or fluorine replace the hydrogen atoms in C–H bond, the band vibration energy is decreased and thus the absorption band is minimized. Thus, we have previously synthesized fluorine containing polystyrene such as poly(2,3,4,5,6-pentafluorostyrene) and poly(4-trifluoromethyl 2,3,5,6-tetrafluorostyrene) [4]. They are thermally stable and transparent, but their glass transition temperatures (T_g) were about 110 °C. However, some applications such as in automobile and airplane require optical polymers with higher T_g (>120 °C) [5–8].

Bomer and Hagemann have synthesized various CF_3 substituted styrenes and their homopolymers. They reported that when CF_3 group substituted on the ortho position of polystyrene, the T_g was considerably higher (175 °C) than those of CF_3 on the meta and para positions whose T_gs were 63 and 101 °C, respectively [9]. This is due to the steric hindrance of the bulky CF_3 group (the Van der Waals volume of CF_3 is 42.6 Å^3 compared to CH_3 with 16.8 Å^3) [10] at the ortho position, which results in a decrease in the segmental mobility of the polymer chains and greatly increases the T_g of the polystyrene. Thus, we have further investigated the CF_3 substituted polystyrenes for possible optical polymer materials with higher T_g. Various fluorine containing styrene monomers (Fig. 1) were synthesized and the polymerization rates of these styrene monomers in benzene and dioxane solutions were measured. Also reported here are the thermal and optical properties of the trifluoromethyl substituted styrenes homopolymers as well as their copolymers with methyl methacrylate and 2,2,2-trifluoroethyl methacrylate.

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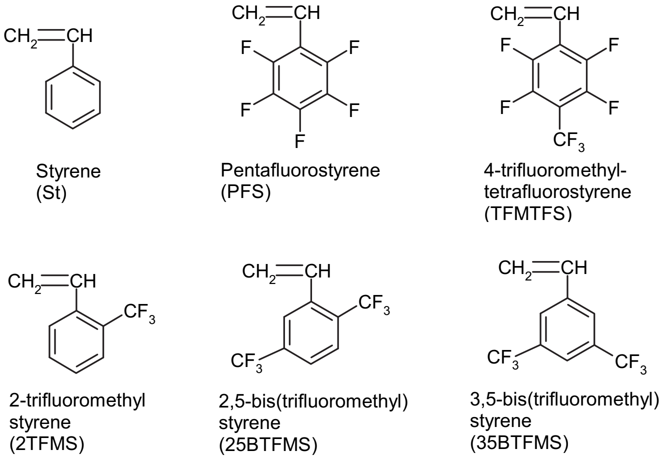


Fig. 1. Chemical structures of styrene monomers investigated.

2. Experimental

2.1. Materials

All solvents, methyl methacrylate (MMA), styrene (St) and 2,2′-azobisisobutyronitrile (AIBN) were purchased from Aldrich. 2,3,4,5,6-Pentafluorostyrene (PFS), 2-trifluoromethyl-bromobenzene, 2,5-bis(trifluoromethyl)-bromobenzene, 3,5-bis(trifluoromethyl)-bromobenzene and 4-trifluoromethyl-2,3,5,6-tetrafluoro-bromobenzene were purchased from SynQuest Co. AIBN was purified through the recrystallization from methanol. All monomers were distilled before use.

2.2. Characterization

^{1}H NMR and ^{19}F NMR spectra were recorded by a Bruker AC 300 spectrometer at 300 and 282 MHz, respectively. Chemical shifts are reported in ppm from internal TMS or $CFCl_3$. The differential scanning calorimetry (DSC) measurement was performed on a DSC 2920 module in conjunction with the TA Instruments 5100 system at a scan rate of 10 °C/min under a nitrogen atmosphere. The instrument was calibrated using indium and zinc as calibration standards for the temperature and enthalpy changes. The midpoint of the heat capacity transition was taken as T_g. Thermogravimetric analysis (TGA) was performed on Hi-Res Modulated TGA 2950 thermogravimetric analyzer under nitrogen at a heating rate of 20 °C/min. The extrapolation of break in the TGA curve was taken as the decomposition temperature (T_d). The molecular weights of polymer samples were determined by gel permeation chromatography (GPC) (Waters 510) using THF as the eluent at a flow rate of 1.0 mL/min. The molecular calibration curves were obtained using polystyrene standards. The refractive indices were measured using a Metricon model 2010 prism coupler, and the measurement accuracy is ±0.0005. The transmittance of polymer films was measured with a UV/VIS spectrometer (Lambda 800, Perkin Elmer, Inc.) at a scanning rate of 100 nm/min. The film thickness was in the range of 110–200 μm.

2.3. Synthesis of styrene monomers

Except for those purchased, styrene monomers were prepared via the dehydration of the related alcohols, which were synthesized by the reaction of corresponding Grignard reagents with acetaldehyde (Scheme 1). In a typical procedure, the Grignard agent was prepared from the related bromide compound and magnesium in anhydrous THF. After slowly adding acetaldehyde, the reaction mixture was treated with diluted hydrochloric acid solution. The resulted alcohol was subjected to distillation under vacuum. The styrene monomers were obtained as a colorless liquid by the elimination of water from alcohols with phosphorous pentoxide, followed by the distillation under vacuum.

2-trifluoromethyl styrene (2TFMS): b.p. 65–66 °C/30 mmHg with a yield of 57%. ^{1}H NMR ($CDCl_3$): 5.30 (dd, $J1 = 1.1$ *Hz*, $J2 = 11.0$ Hz, 1H), 5.66 (d, $J = 17.2$ Hz, 1H), 7.00 (m, 1H), 7.30–7.70 (m, 4H). ^{19}F NMR ($CDCl_3$): −59.5 (s, 3F).

2,5-bis(trifluoromethyl) styrene (25BTFMS): b.p. 70–71 °C/30 mmHg with a yield of 60%. ^{1}H NMR ($CDCl_3$): 5.43 (dd, $J1 = 0.6$ *Hz*, $J2 = 11.1$ Hz, 1H), 5.80 (d, $J = 17.2$ Hz, 1H), 7.00 (m, 1H), 7.60–7.90 (m, 3H). ^{19}F NMR ($CDCl_3$): −60.2 (s, 3F), −63.3 (s, 3F).

3,5-bis(trifluoromethyl) styrene (35BTFMS): b.p. 72–73 °C/30 mmHg with a yield of 55%. ^{1}H NMR ($CDCl_3$): 5.49 (d, $J = 11.0$ *Hz*, 1H), 5.90 (d, $J = 17.6$ Hz, 1H), 6.77 (dd, $J1 = 11.0$ Hz, $J2 = 17.6$ Hz, 1H), 7.70–7.90 (m, 3H). ^{19}F NMR ($CDCl_3$): −63.2 (s, 6F).

4-trifluoromethyl-2,3,5,6-tetrafluorostyrene (TFMTFS): b.p. 36–37 °C/20 mmHg with a yield of 58%. ^{1}H NMR ($CDCl_3$): 5.87 (d, $J = 11.8$ Hz, 1 H), 6.24 (d, $J = 17.9$ Hz, 1H), 6.71 (dd, $J = 11.8$ Hz, $J = 17.9$ Hz, 1H). ^{19}F NMR ($CDCl_3$): −56.37 (m, 3 F), −141.86 (m, 4F).

2.4. Polymerization

Polymerizations were carried out in bulk for the general characterization purpose, or in benzene and dioxane solutions for kinetics study. AIBN was used as the free radical initiator in all the polymerizations. Monomers and initiator were transferred into a glass tube, which was subject to three times of the freeze–pump–thaw cycles and followed by sealing with flame under vacuum. After polymerizing in a water bath at 60–80 °C for 20–30 h, the tube was opened carefully, and the content was purified by the precipitation from THF solution to a large amount of methanol or hexane. The polymer collected was dried in vacuum oven at 60 °C for 48 h.

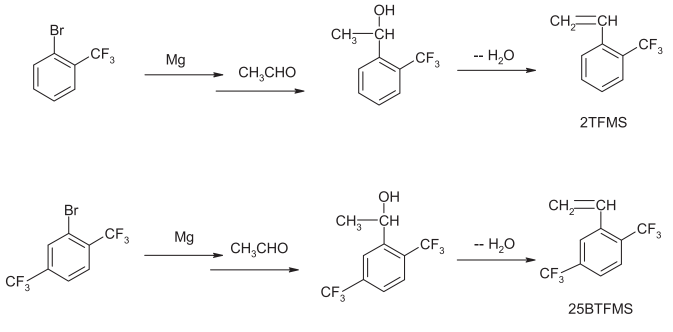
2.5. Kinetics

The polymerization rate can be expressed as following equations [11]:

$$R_p = k_p\left(\frac{fk_d}{k_t}\right)^{1/2}[I]^{1/2}[M] \tag{1}$$

$$\ln\frac{[M]_0}{[M]} = k[I]^{1/2}t \tag{2}$$

where R_p is the polymerization rate, k_p is the propagation rate coefficient, f is the initiator decomposition efficiency, k_d is the



Scheme 1. Synthesis routes for the preparation of substituted styrene monomers.

initiator decomposition rate coefficient, k_t is the termination rate coefficient, $[I]$ is the initiator concentration, $[M]$ is the monomer concentration, k is the observed polymerization rate coefficient, and t is the polymerization time. The change of the monomer concentration could be monitored by ^{1}H NMR measurements of the double bond protons (Fig. 2).

2.6. Reactivity ratio

The reactivity ratios of each pair of comonomers in a copolymerization were calculated according to the Mayo–Lewis method [12].

3. Results and discussion

The CF_3 substituted styrenes were readily polymerized in bulk and also in solutions using AIBN as a free radical initiator. To study the effect of the F and CF_3 substitution on the activity of related styrene monomers, the polymerization kinetics was carried out in nonpolar solvent benzene and polar solvent dioxane. To obtain accurate results, the solvents used in kinetics study were purified carefully with the traditional methods. The polymerization rate was monitored by measuring the double bond protons in monomers (Fig. 2). The observed polymerization rate coefficient k was calculated according to Eqn. (2) (Table 1). It was found that the polymerization is faster in a polar solvent such as dioxane than in a less polar solvent such as benzene, which is agreeing to the literature results [13].

The free radical initiated polymerization of styrene has been widely investigated [14–17]. The head to tail placement would be expected to be overwhelmingly predominant, since successive propagating radicals formed by the attachment of a radical at the β carbon of the double bond is more stable due to the resonance effects of the phenyl group and less steric hindrance. The situation with substitution on the benzene ring of substituted styrene monomers should be the same.

As shown in Fig. 2, when X has a more electron-withdrawing property, such as Cl and CN, the polymerization rate of the monomer was found to be faster than those of X having an electron donating property, such as CH_3 and OCH_3 [18]. The polymerization rates of para substituted styrenes were following a Hammett σ–ρ relationship [19].

The protons in nonfluorinated styrene appeared in the upper field in NMR spectrum as comparing to those in fluorosubstituted styrenes due to the electron-withdrawing property of F and CF_3 (Fig. 3). The protons in TFMTFS appeared at a lower field than those of PFS because the CF_3 group is a more electron-withdrawing group than the F atom. To reveal the structure and activity relationship, the chemical shifts of the proton H^2 were plotted against the polymerization rate coefficients of these styrene monomers, and a linear relationship was found as shown in Fig. 4. Besides the solvent effect as mentioned above, the polymerization rates of these styrene monomers were in the decreasing order of TFMTFS > 35BTFMS > 25BTFMS > PFS > 2TFMS > St.

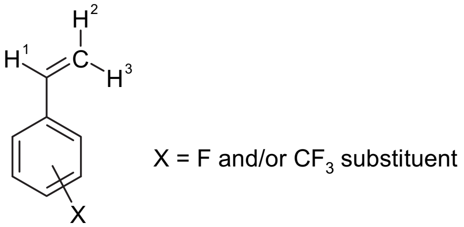


Fig. 2. Proton identification of the substituted styrene monomers.

Table 1
Polymerization rate constants of styrene monomers at 50 °C.

	k (benzene) ($\times 10^{-5}$ L$^{1/2}$/mol$^{1/2}$ S)	k (dioxane) ($\times 10^{-5}$ L$^{1/2}$/mol$^{1/2}$ S)	T_g(°C)
St	2.4	4.0	105
PFS	4.8	9.8	108
TFMTFS	8.7	16	112
2TFMS	3.1	6.1	165
25BTFMS	7.7	10	160
35BTFMS	6.1	15	116

It can be seen that the more the electron-drawing substitution, the more active the monomer is. The polymerization rates of fluorinated styrene are faster than that of regular styrene because of this polarity effect [20]. The CF_3 substitution at the para position of TFMTFS has much stronger polarity effect when comparing with the F substitution at the same position in PFS. When X is CF_3 group, the Hammett constant σ_p is 0.54, where ρ was calculated as 0.6. While X is F atom only, the Hammett constant σ_p is 0.062 [21]. It can be seen that there is a big difference between CF_3 and F substitutions at the para position of the benzene ring, which could explain the big difference between the polymerization activities of PFS and TFMTFS. The polymerization rate of 25BTFMS is much slower than that of 35BTFMS due to the steric effect of the CF_3 group at the ortho position of 25BTFMS.

T_gs of 2TFMS, 25BTFMS and 35BTFMS homopolymers were 165, 160 and 116 °C [22], respectively, and T_gs of PFS and TFMTFS homopolymers were 108 and 112 °C, respectively (Table 1). As can be seen, T_gs of polymers with CF_3 substituted at the ortho position of the phenyl ring are much higher in comparison with P35BTFMS. This is due to the steric hindrance of the bulky CF_3 group near the polymer main chain, which resulted in a decreased segmental mobility of the polymer chains and the increased T_g of the polymers.

Comparing with homopolymers, copolymer systems produce more variable properties. Generally, the copolymerization can decrease the crystallinity and increase the flexibility of the polymer materials. Styrene polymers have higher thermal and chemical stabilities. While they exhibit poor mechanical properties and are difficult to prepare thin fibers due to the rigid polymer structure. Comparatively, acrylate polymers showed excellent processing properties, while they can be only utilized at a low temperature environment due to the low T_g. The combination of the positive properties from styrene polymers and acrylate polymers would be an ideal result. However, as optical materials, copolymers tend to have extremely high light scattering loss due to the large heterogeneous macromolecular structure and the corresponding

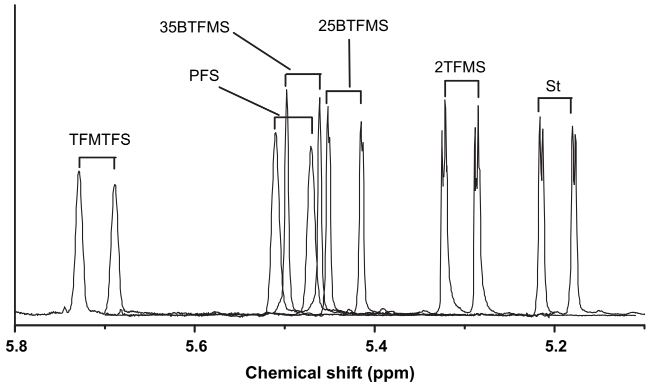


Fig. 3. ^{1}H NMR spectra for the H^2 protons of the double bonds in styrene monomers.

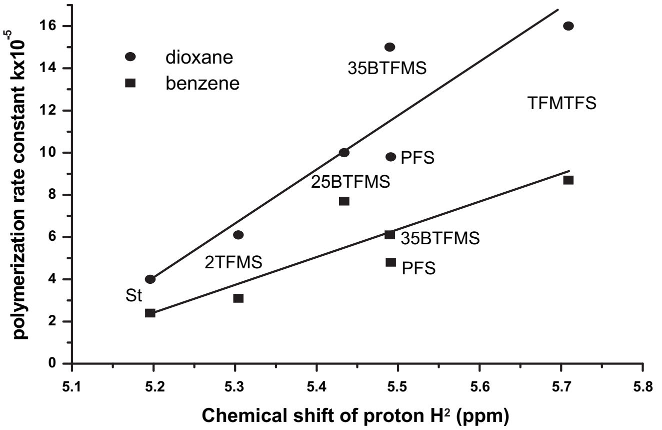


Fig. 4. Relationship of the polymerization rate constants and the chemical shifts of H^2 protons.

heterogeneity of the refractive index distribution. Consequently, copolymers have not been the leading candidate for photonic materials.

The copolymerization reactivity ratios r_1 and r_2 were found to be 0.84 and 1.55 for MMA and 2TFMS, respectively (Table 2), which indicate that these two monomers produce copolymers with the random composition. The refractive indices of poly(2TFMS) and PMMA are 1.51 and 1.50 at 532 nm, respectively. The very close refractive indices of the different polymeric units could minimize the light scattering. Combining the random copolymer chain structure characteristics, the transparent copolymer could be produced from the two monomers. The same situation is in the case of the trifluoroethyl methacrylate (TFEMA) and 25BTFMS system. The copolymerization reactivity ratios r_1 and r_2 are 0.64 and 1.18 for TFEMA and 25BTFMS, respectively. The refractive indices of poly (25BTFMS and PTFEMA) are 1.45 and 1.44 at 532 nm, which are also very close to each other. Therefore, these copolymers may exhibit no light scattering [23]. Thus, the copolymers of MMA with 2TFMS and also the copolymers of TFEMA with 25BTFMS were prepared for possible novel optical applications (Table 3).

These copolymers exhibit a single glass transition temperature, which indicates that they have a random homogeneous macromolecular structure (Table 3). T_gs of the copolymers are dependent on their composition and follow a linear relationship as shown in Fig. 5. This makes it possible to design the copolymers with different refractive indices for different applications. In comparison to the low T_g of methacrylate polymers and the poor mechanical properties of the styrene polymers, these copolymers offer the higher T_g (>130 °C) required for special applications of optical polymers in high temperature environment [5–8], while maintaining the excellent processability.

The copolymers were found to degrade at above 310 °C in TGA measurements, which means these copolymers are thermally stable in comparison with MMA and TFEMA homopolymers and are capable to the general fiber preparation procedure at 200–300 °C. The data in Table 3 also showed that copolymers have higher molecular weight in comparison to the homopolymers. This high molecular weight is precious for the special preparation method for the gradient index plastic optical fiber (GI-POF), since it is necessary to add dopants and chain transfer agents in the system during the preparation, while keeping the good mechanical properties of the polymer material [24,25].

Table 2
The monomer reactivity ratios of comonomer pair.

M_1/M_2	r_1	r_2	r_1r_2
MMA/2TFMS	0.84 ± 0.04	1.55 ± 0.08	1.30
TFEMA/25BTFMS	0.64 ± 0.03	1.18 ± 0.06	0.76

Table 3
Thermal analysis and molecular weight results.

Sample	Composition (wt%)	T_g (°C)	T_d (°C)	M_w	M_n
1	MMA	108	338	101.000	39.500
2	MMA/2TFMS = 74/26	127	312	–	–
3	MMA/2TFMS = 50/50	136	341	337.700	99.200
4	MMA/2TFMS = 26/74	146	338	–	–
5	2TFMS	165	382	193.100	59.700
6	TFEMA	75	280	241.600	86.200
7	TFEMA/25BTFMS = 76/24	86	311	–	–
8	TFEMA/25BTFMS = 51/49	103	322	344.400	89.300
9	TFEMA/25BTFMS = 25/75	129	332	–	–
10	25BTFMS	160	366	266.300	88.800

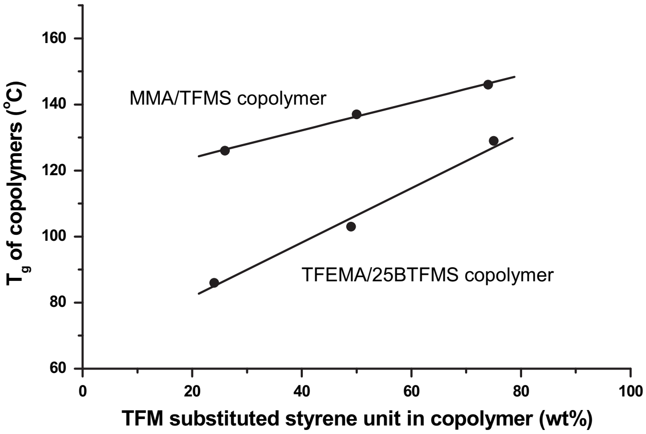


Fig. 5. Composition dependence of T_gs for MMA/2TFMS and TFEMA/25BTFMS copolymers.

The refractive indices of the copolymers from methacrylates and CF_3 substituted styrenes were studied at different wavelengths (532 nm, 633 nm, 839 nm), and the composition dependence of the refractive index was plotted in Fig. 6. The results show that there is a linear relationship between the refractive indices of the copolymers and their compositions. It suggests that there is no macrophysical property change such as density, which may occur during the

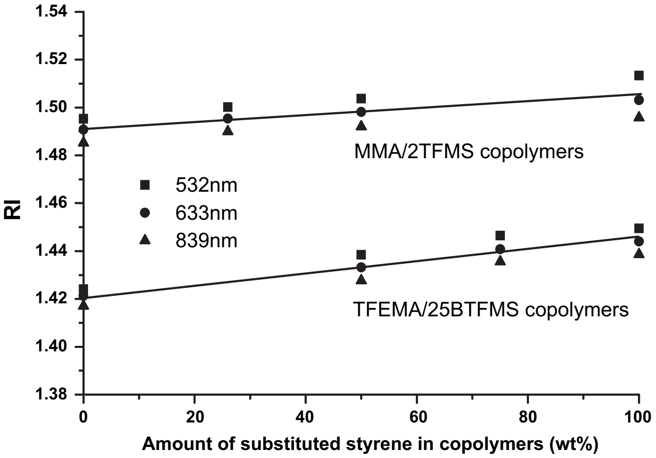


Fig. 6. Composition dependence of the refractive index for copolymer systems.

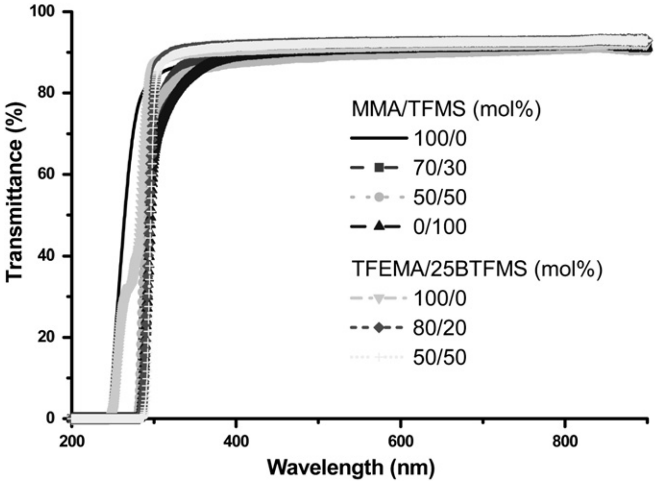


Fig. 7. Transmittance spectra of MMA/2TFMS and TFEMA/25BTFMS copolymer systems.

formation of the copolymers. This is agreeing with the conclusion of the homogeneous macromolecular structure from the T_g results.

Fig. 7 showed that these copolymer films (110–200 μm) exhibit similar transmittance (~90%) as the homopolymers of MMA and TFEMA in the 300–900 nm wavelength range. This high transmittance should result from the random copolymer composition due to the similar reactivity ratio of the two monomers and the negligible light scattering due to the similar refractive indices of the two monomeric units in the polymer chains. Since most copolymers have high light scattering due to the heterogeneous macromolecular structure, these transparent copolymers are combining the excellent mechanical properties of acrylate polymers, high thermal stability of styrene polymers and the desired optical properties similar to amorphous homopolymers.

4. Conclusion

Homopolymers of 2TFMS and 25BTFMS, as well as their copolymers with MMA and TFEMA, exhibited relatively high T_gs, high thermal stability and high transmittance. These polymers may be utilized as novel optical materials.

References

[1] Ziemann O, Krauser J, Zamgow PE, Daum W. POF Handbook. 2nd ed. Berlin: Springer; 2008. 166–168.
[2] Groh W. Makromol Chem 1988;189:2861–70.
[3] Groh W. Macromolecules 1991;24:6660–8.
[4] Lou L, Koike Y, Okamoto Y. J Polym Sci Part A Polym Chem 2010;48:4938–42.
[5] Truong TK. Commercial airplane fiber optics needs, opportunities, challenges, the 19th International Conference on Plastic Optical Fibers, Japan, October 2010.
[6] Ziemann O, Krauser J, Zamgow PE, Daum W. POF Handbook. 2nd ed. Berlin: Springer; 2008. 157–158.
[7] Koike K, Koike Y. J Lightw Technol 2009;27:41–6.
[8] Sato M, Hirai M, Ishigure T, Koike Y. J Lightw Technol 2000;18:2139–45.
[9] Boner B, Hagemann H. Angew Makro Chem 1982;109:285–93.
[10] Chambers RD. Fluorine in Organic Chemistry. CRC Press; 2000. p 92.
[11] Odian G. Principles of polymerization. 2nd ed. John Wiley and Sons; 1981. pp. 197–199.
[12] Mayo FR, Lewis FM. J Am Chem Soc 1944;66:1594–601.
[13] Beuermann S, Buback M. Progr Polym Sci 2002;27:191–254.
[14] Coote ML, Davis TP. Macromolecules 1999;32:4290–8.
[15] Buback M, Garcia-Rubio L, Gilbert R, Napper D, Guillot J, Hamielec A, et al. J Polym Sci Part C Polym Lett 1988;26:293–7.
[16] Mahabadi HK. Macromolecules 1985;18:1319–24.
[17] Walling C, Briggs ER, Wolfstirn BK, Mayo FR. J Am Chem Soc 1948;70: 1537–42.
[18] Imoto M, Kinoshita M, Nishigaki M. Makro Chem; 1965:217–30.
[19] Pryor W, Huang TL. Macromolecules 1962;2:70–7.
[20] Hammett Louis P. Chem Rev 1935;17:125–36.
[21] Hansch C, Leo A, Taft RW. Chem Rev 1991;91:165–95.
[22] The T_g of 35BTFMS homopolymer was reported as 60 °C in reference [6].
[23] Koike K, Kado T, Satoh Z, Okamoto Y, Koike Y. Polymer 2010;51:1377–85.
[24] Koike K, Teng H, Okamoto Y, Koike Y. Proc ICPOF; 2007:318–9.
[25] Koike Y, Koike K. J Polym Sci Part B Polym Phys 2011;49:2–17.