

Property modification of poly(methyl methacrylate) through copolymerization with fluorinated aryl methacrylate monomers

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Copolymers of methyl methacrylate (MMA) with 2,3,5,6-tetrafluorophenyl methacrylate (TFPMA), pentafluorophenyl methacrylate (PFPMA), and 4-trifluoromethyl-2,3,5,6-tetrafluorophenyl methacrylate (TFMPMA) were investigated. All the three systems showed a random copolymerization character. The composition, glass transition temperature (T_g), and refractive index of the copolymers obtained were studied. T_g s of TFPMA/MMA and PFPMA/MMA copolymers were found to deviate positively from the Gordon–Taylor equation. However, T_g s of TFMPMA/MMA copolymers were well fit with the Gordon–Taylor equation. These results indicated the existence of interaction between MMA and either TFPMA or PFPMA units in copolymers. This interaction resulted in the enhancement of the T_g of MMA polymers through the copolymerization with TFPMA and PFPMA. The refractive index and the light transmittance of copolymers were close to those of PMMA. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: poly(methyl methacrylate); modification; copolymerization; fluoropolymers; T_g

INTRODUCTION

Poly(methyl methacrylate) (PMMA) is a commercially important polymer with high light transmittance, colorlessness, and excellent chemical and weather corrosion resistances.¹ The favorable physical properties of PMMA, coupled with ease of processing, make PMMA a widely used substitute for glass in optical device applications.² However, the major disadvantage of PMMA is its relatively low glass transition temperature (T_g) (about 100°C) and high water absorption, which limit its utility for optical electronic applications.^{3,4}

Poly(aryl methacrylate)s have relatively higher T_g due to the enhanced rigidity of the aromatic ring-containing polymeric chains.⁵ Aryl methacrylates are easily copolymerized with most of the known monomers, which allows broad modifications for polymer properties. In order to increase T_g of PMMA, investigators have explored its copolymerization with rigid or bulky aryl methacrylate monomers.^{6–8} MMA has also been copolymerized with monomers containing groups which can form hydrogen-bonding interactions with the carbonyl group of MMA.^{9,10} Unfortunately, both

types of modifications tend to decrease the transparency or humidity resistance of the copolymers obtained.

For PMMA, in the visible to near infrared region, light losses are dominated by C–H overtone stretches and combinations of stretch overtones and deformation vibrations. When heavier atoms such as deuterium or fluorine replace the hydrogen atom in C–H bonds, the band vibration energy is decreased, and thus the absorption band is minimized in the region of the visible to near infrared. Boutevin *et al.*¹¹ have prepared several fluorine-substituted acrylate monomers and their polymers as highly transparent organic materials.

Fluorine is the most electronegative element, and the fluorine-substituted phenyl moiety tends to form complexes with electron donating groups such as aromatic hydrocarbons and amines.^{12,13} Some interaction between ester groups and fluorinated phenyl groups is also expected.¹⁴ Generally, the inclusion of fluorinated groups into the polymer structure will increase the thermal stability, flame retardancy, oxidation resistance, humidity resistance, and transparency.¹⁵

Thus, in order to increase the T_g of PMMA and to maintain its transparency, here are reported the preparation of the fluorinated phenyl methacrylates, 2,3,5,6-tetrafluorophenyl methacrylate (TFPMA), pentafluorophenyl methacrylate

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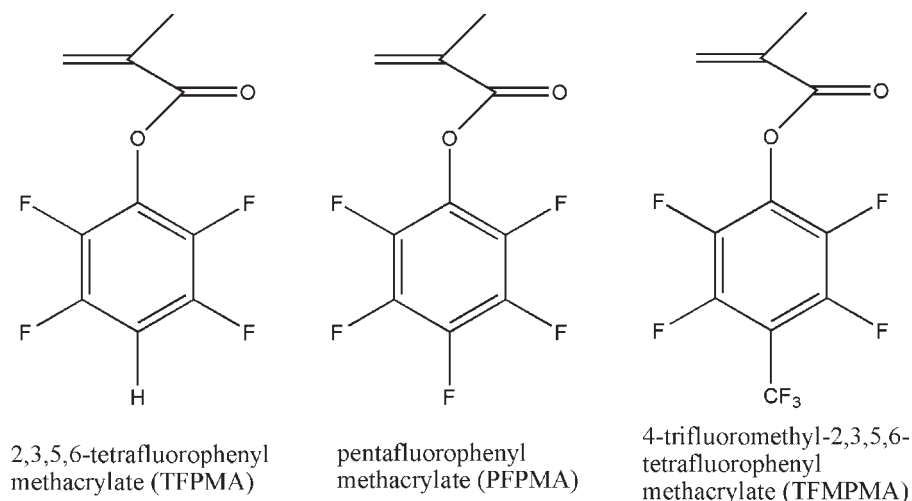


Figure 1. Chemical structures of fluorinated phenyl methacrylates.

(PFPMA), and 4-trifluoromethyl-2,3,5,6-tetrafluorophenyl methacrylate (TFMPMA) (Fig. 1) and the investigation of the thermal as well as optical properties of their copolymers with MMA.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA), methacryloyl chloride, pyridine, diethyl ether, tetrahydrofuran (THF), chloroform, and azobis(isobutyronitrile) (AIBN) were purchased from Aldrich. Pentafluorophenol, 2,3,5,6-tetrafluorophenol, and 4-trifluoromethyl-2,3,5,6-tetrafluorophenol were purchased from SynQuest Co. Diethyl ether and THF were distilled over calcium hydride (CaH₂) and the free radical initiator AIBN was purified by recrystallization from methanol. Monomers were purified with traditional method. All other chemicals were used directly without further purification.

Monomer synthesis

TFPMA: 50 g of 2,3,5,6-tetrafluorophenol (0.30 mol) was dissolved in 800 ml of ether. After cooling the solution with ice/water bath, 24 g of pyridine (0.30 mol) was added slowly. Then, the solution of 32 g of methacryloyl chloride (0.31 mol) in 400 ml of ether was dropped slowly into the above cooled solution. After stirring for 5 hr at room temperature and 2 hr at 50°C, the reaction was stopped and the white precipitate was filtered off and washed with ether. The combined ether solutions were washed with 3% hydrochloric acid, saturated sodium chloride solution, and 3% sodium bicarbonate. After drying with anhydrous magnesium sulfate, the ether solution was filtered and concentrated with a rotary evaporator. A colorless liquid was obtained by distillation at 61°C/5 mmHg with a yield of 80%. ¹H NMR (CDCl₃): 2.1 (s, 3H), 5.9 (s, 1H), 6.5 (s, 1H), 7.0 (m, 1H); ¹³C NMR (CDCl₃): 18.3, 103.2, 129.8, 130.1, 134.0, 140.9, 146.2, 163.2; ¹⁹F NMR (CDCl₃): -139.7 (m, 2F), -153.6 (m, 2F).

Phenyl methacrylate (PMA), PFPMA, and TFMPMA were prepared using a similar method described above. For PMA, b.p. 69°C/1 mmHg; ¹H NMR (CDCl₃): 1.9 (s, 3H), 5.5 (s, 1H), 6.0 (s, 1H), 7.2 (m, 5H); ¹³C NMR (CDCl₃): 18.0, 121.6, 125.6, 128.0, 129.2, 135.4, 151.4, 166.0. For PFPMA, b.p. 56°C/

3 mmHg; ¹H NMR (CDCl₃): 2.1 (s, 3H), 5.9 (s, 1H), 6.5 (s, 1H); ¹³C NMR (CDCl₃): 18.4, 125.8, 130.1, 134.1, 136.6, 140.0, 143.3, 163.4; ¹⁹F NMR (CDCl₃): -153.4 (m, 2F), -158.9 (t, 1F), -163.1 (m, 2F). For TFMPMA, b.p. 102°C/8 mmHg; ¹H NMR (CDCl₃): 2.1 (s, 3H), 5.9 (s, 1H), 6.5 (s, 1H); ¹³C NMR (CDCl₃): 18.2, 107.5, 130.5, 133.1, 133.7, 139.8, 143.1, 146.5, 162.6; ¹⁹F NMR (CDCl₃): -56.6 (t, 3F), -141.2 (m, 2F), -151.0 (m, 2F).

Polymerization

AIBN was employed as an initiator. The monomer mixtures, including known amounts of comonomers and initiator, were transferred into a glass polymerization tube, which was subjected to repeated freeze-pump-thaw cycles and sealed under vacuum. After polymerization was finished, the glass tube was opened and the content was poured into a large amount of methanol with vigorous stirring to precipitate the polymer. After drying under vacuum at 50°C for 24 hr, polymer samples were re-precipitated from chloroform into methanol. The purified polymer samples were dried under vacuum at 50°C for 48 hr.

Characterizations

¹H, ¹³C, and ¹⁹F NMR spectra were taken using a Bruker ACF 300 spectrometer (300 MHz for ¹H NMR, 75 MHz for ¹³C NMR, and 282 MHz for ¹⁹F NMR measurements). Molecular weights were determined by gel permeation chromatography (GPC) (Waters 510) using chloroform as an eluent at a flow rate of 1.0 ml/min. The molecular weight calibration curve was obtained using polystyrene standards. The glass transition temperature (*T*_g) of polymers was measured using a DSC 2920 module with the TA Instrument 5100 system, with a scan rate of 10°C/min. The *T*_g is taken in the second heating scan as the midpoint of the heat capacity transition between the upper and lower points of deviation from the extrapolated liquid and glass lines. The polymer films (0.1–0.2 mm thick) fabricated by casting the solutions on glass plates were used to measure the refractive index, using a prism coupler (Metricon, modul 2010). The measurement accuracy was ±0.0005. The probe wavelengths in the prism were 532 and 839 nm. Transmittance measurements were recorded on a Shimadzu UV-2401PC spectrophotometer.

Table 1. Homopolymerizations of PFPMA and TFPMA

Run	Monomer ^a	[CTA]/[M] ^b	Time (hr)	Conv. ^c (wt%)	M_w ($\times 10^4$)
1	PFPMA	0.01 ^d	26	83	6.5
2	PFPMA	0.03 ^d	26	76	2.2
3	PFPMA	0.01 ^e	18	80	7.0
4	TFPMA	0.01 ^e	48	95	9.0
5	TFPMA	0.02 ^e	48	95	7.0
6	TFPMA	0.03 ^e	48	90	6.5

^a The ratio of initiator/monomer $[I]/[M] = 0.01$; polymerization temperature, 60°C.

^b The ratio of chain transfer agent (CTA)/monomer.

^c The conversion of monomer by gravimetry.

^d $n\text{-C}_{12}\text{H}_{25}\text{SH}$ as CTA.

^e $n\text{-C}_4\text{H}_9\text{SH}$ as CTA.

RESULTS AND DISCUSSION

Homopolymerizations of PFPMA and TFPMA were carried out in bulk considering the requirement of optical fiber processing. Without a chain transfer agent (CTA), polymers obtained had too high molecular weight and often were not soluble in common organic solvents such as chloroform and THF. Thus, the CTAs, $n\text{-C}_{12}\text{H}_{25}\text{SH}$ and $n\text{-C}_4\text{H}_9\text{SH}$, were used to adjust the molecular weight of polymers. The typical data of homopolymerizations are summarized in Table 1. It can be seen that the molecular weight of polymers could be adjusted effectively with these CTAs.

The copolymerizations of TFPMA and MMA were carried out with various comonomer feed ratios (Table 2). In order to determine monomer reactivity ratios, the conversion of polymerization was controlled below 10 wt%. The copolymer compositions were determined by $^1\text{H-NMR}$ measurements and monomer reactivity ratios were calculated according to the Fineman–Ross method.¹⁶ All the copolymers obtained were soluble in chloroform and the data showed that the molecular weights of copolymers were high enough for optical fiber processing. The refractive index of copolymers obtained was very close to that of PMMA.

Determined monomer reactivity ratios, r_1 (TFPMA) and r_2 (MMA), were 1.47 ± 0.05 and 0.77 ± 0.01 , respectively, and $r_1 \times r_2$ equaled 1.13. This shows that these monomers have good copolymerization properties and yield random copolymers. A plot of the copolymer T_g versus the composition (Fig. 2) deviated from a linear relationship described by the Gordon–Taylor equation (Eqn 1):¹⁷

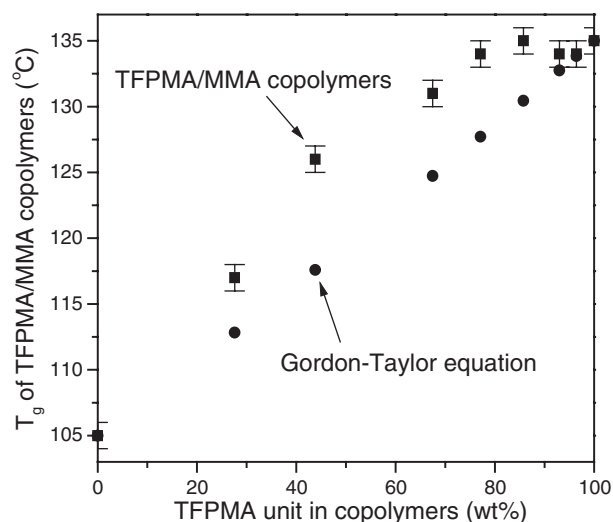
$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \quad (1)$$

where w_1 and w_2 are weight fractions of the two monomeric units in the copolymer, T_{g1} and T_{g2} are T_g s of related

Table 2. Characterizations of TFPMA/MMA copolymers

Run ^a	TFPMA feed (mol%)	TFPMA unit in copolymer (mol%)	M_n ($\times 10^4$)	M_w ($\times 10^4$)	n_d	
					532 nm	839 nm
1	0	0	—	—	1.4953	1.4852
2	11	14	12.42	31.49	1.4956	1.4853
3	20	25	15.60	33.42	1.4959	1.4855
4	35	47	18.69	40.18	1.4968	1.4859
5	89	92	—	—	1.4990	1.4862
6	100	100	—	—	1.4992	1.4860

^a $[I]/[M] = 0.01$; polymerization temperature, 60°C; polymerization conversion ≤ 10 wt%.

**Figure 2.** Composition dependence of glass transition temperatures for TFPMA/MMA copolymers.

homopolymers, and k is a fitting constant. The deviation indicated that there is some interaction between the polymer chains, which confined the mobility of the polymer segments and resulted in the enhanced T_g .

The copolymerizations of PFPMA and MMA with various comonomer feed ratios were also carried out and the results were summarized in Table 3.

Monomer reactivity ratios, r_1 (PFPMA) and r_2 (MMA), were found to be 1.20 ± 0.09 and 0.51 ± 0.06 , respectively. These results indicated that these monomers also tend to form random copolymers. T_g s of the PFPMA/MMA copolymers were also found to deviate positively from linear relationship expected from the Gordon–Taylor equation (Fig. 3). This should be the result of the similar interaction between polymer chains as in TFPMA/MMA system.

Table 3. Characterizations of PFPMA/MMA copolymers

Run ^a	PFPMA feed (mol%)	PFPMA unit in copolymer (mol%)	n_d	
			532 nm	839 nm
1	0	0	1.4953	1.4852
2	10	15	1.4936	1.4835
3	20	32	1.4927	1.4827
4	50	61	1.4910	1.4809
5	100	100	1.4894	1.4763

^a $[I]/[M] = 0.01$; polymerization temperature, 60°C; polymerization conversion ≤ 10 wt%.

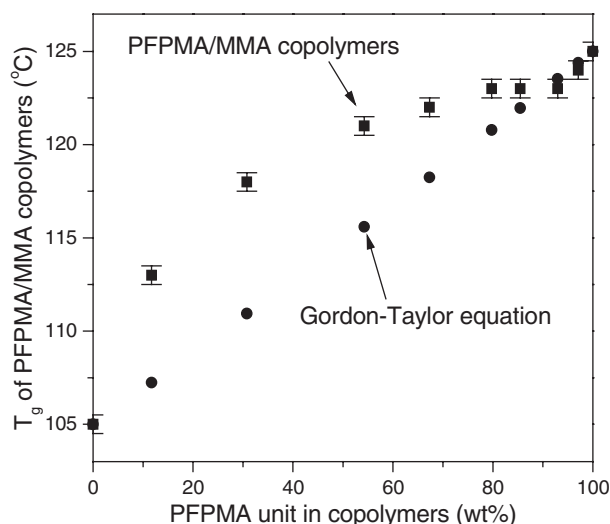


Figure 3. Composition dependence of glass transition temperatures for PFPMA/MMA copolymers.

To compare the results obtained above, the copolymerizations of another fluorinated monomer, TFMPMA (Table 4), and a non-fluorinated monomer, PMA, with MMA were also carried out. The composition dependences of copolymer T_g s for these two systems were plotted in Figs. 4 and 5, respectively.

Monomer reactivity ratios obtained, r_1 (TFMPMA) and r_2 (MMA), were 1.15 ± 0.02 and 0.86 ± 0.01 , respectively, and $r_1 \times r_2$ equaled 1.29. For PMA/MMA system, r_1 (PMA) and r_2 (MMA), were 1.18 ± 0.04 and 0.65 ± 0.03 , respectively, and $r_1 \times r_2$ equaled 0.77. Both of the two systems showed a random copolymerization character. While, the T_g s of TFMPMA/MMA and PMA/MMA copolymers were fit well with the relationship of compositions from the Gordon–Taylor equation (Figs. 4 and 5). These results are different from those obtained in the copolymerization systems of TFPMA/MMA and PFPMA/MMA. Possibly, the trifluoro-methyl substituted fluorinated phenyl group is bulkier than the non-substituted one, so that the interaction between polymer chains might be inhibited. In the case of PMA/MMA copolymer system, the phenyl group is not polarized enough to form some interaction between polymer chains. Therefore, the absence of the interaction in both of these two systems gave the similar results that T_g s of the copolymers were fit with the relationships of compositions as predicted by the Gordon–Taylor equation. These possibilities are currently under further investigation.

Table 4. Characterizations of TFMPMA/MMA copolymers

Run ^a	TFMPMA feed (mol%)	TFMPMA unit in copolymer (mol%)	n_d	
			532 nm	839 nm
1	0	0	1.4953	1.4852
2	10	19	1.4867	1.4767
3	25	40	1.4782	1.4681
4	100	100	1.4637	1.4514

^a $[I]/[M] = 0.01$; polymerization temperature, 60°C; polymerization conversion ≤ 10 wt%.

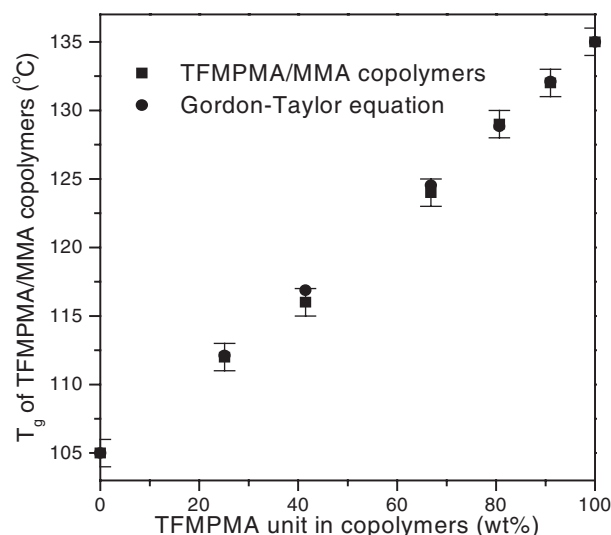


Figure 4. Composition dependence of glass transition temperatures for TFMPMA/MMA copolymers.

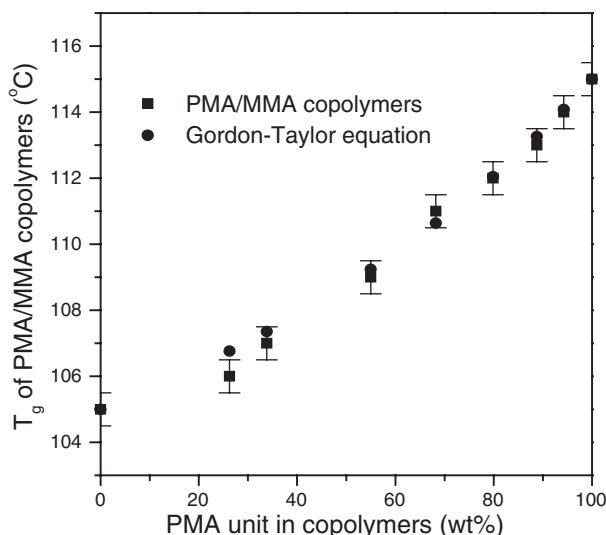


Figure 5. Composition dependence of glass transition temperatures for PMA/MMA copolymers.

It should be mentioned that the refractive indexes of copolymers from all three fluorinated PMA/MMA systems were very close to that of MMA homopolymer. This result is very important for the application of copolymers as optical materials, because light loss caused by light scattering would be minimized. Transmittance measurements of these copolymers were obtained and the results showed that the transmittance of copolymers containing fluorinated monomers was similar to that of MMA homopolymer and independent of the wavelength over the range of 800–900 nm.

CONCLUSIONS

The copolymer T_g s were found to deviate positively from the linear relationship by the Gordon–Taylor equation in PFPMA/MMA and TFPMA/MMA systems, while for TFMPMA/MMA and PMA/MMA systems the data fitted well with the equation. The results indicated that there is an interaction between the PFPMA/MMA and TFPMA/MMA

copolymer chains. The thermal property of MMA polymers was enhanced through the copolymerization with fluorinated aryl monomers, TFPMA and PFPMA, while retaining desirable optical properties similar to those of MMA homopolymer.

REFERENCES

1. Yuichi K, Kazuo K, Koichi N. Synthesis of *N*-cyclohexylmaleimide for heat-resistant transparent methacrylic resin. *J. Appl. Polym. Sci.* 1997; **63**: 363–368.
2. Losch K. Optical polymers for telecom applications. *Macromol. Symp.* 1995; **100**: 65–69.
3. Otsu T, Matsumoto A, Kubota T, Mori S. Reactivity in radical polymerization of *N*-substituted maleimides and thermal stability of the resulting polymers. *Polym. Bull.* 1990; **23**: 43–50.
4. Braun D, Czerwinski WK. Kinetische analyse der copolymerisationsgeschwindigkeit von *N*-vinyl-2-pyrrolidon mit styrol und methylnmethacrylat. *Makromol. Chem.* 1987; **188**: 2389–2401.
5. Syromyatnikov VG, Paskal LP, Savchenko IA. Aryl (meth)acrylates and polymers based on them. *Russ Chem Rev* 1999; **68**: 781–799.
6. Tan Y, Ekenstein G. (2,6-Diphenyl) phenyl methacrylate. *Eur. Polym. J.* 1994; **30**: 1363–1366.
7. Mishra A, Sinha T, Choudhary V. Methyl methacrylate-*N*-chlorophenyl maleimide copolymers: effect of structure on properties. *J. Appl. Polym. Sci.* 1998; **68**: 527–534.
8. Dong S, Wei Y, Zhang Z. Study on the synthesis of heat-resistant PMMA. *J. Appl. Polym. Sci.* 1999; **72**: 1335–1339.
9. Pearce EM, Kwei TK, Min BY. Polymer compatibilization through hydrogen bonding. *J. Macromol. Sci. Chem.* 1984; **A21**: 1181–1216.
10. Kuo S, Kao H, Chang F. Thermal behavior and specific interaction in high glass transition temperature PMMA copolymer. *Polymer* 2003; **44**: 6873–6882.
11. Boutevin B, Rousseau A, Bosc D. Accessible new acrylic monomers and polymers as highly transparent organic materials. *J. Polym. Sci., Polym. Chem.* 1992; **30**: 1279–1286.
12. Chambers RD. *Fluorine in Organic Chemistry*. CRC press: FL, USA, 2004; chapter 9.
13. Beaumont TG, Davis KMC. Multiple charge transfer bands in complexes of hexafluorobenzene with aromatic amines. *Nature* 1968; **218**: 865.
14. Jennings WB, Farrell BM, Malone JF. Attractive intramolecular edge-to-face aromatic interactions in flexible organic molecules. *Acc. Chem. Res.* 2001; **34**: 885–894.
15. Ameduri B, Boutevin B. *Well-Architected Fluoropolymers: synthesis, Properties and Applications*. Elsevier Ltd: Amsterdam, 2004; 3.
16. Fineman M, Ross SD. Linear method for determining monomer reactivity ratios in copolymerization. *J. Polym. Sci.* 1950; **5**: 259–262.
17. Gordon M, Taylor JS. Ideal copolymers and the second-order transitions of synthetic rubbers. I. Non-crystalline copolymers. *J. Appl. Chem.* 1952; **2**: 493–500.