Free Radical Copolymerization of *tert*-Butyl 3-Isopropenylcumylperoxide with Styrene and Grafting of Methyl Methacrylate onto the Copolymers

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ABSTRACT: Copolymers of *tert*-butyl-3-isopropenylcumylperoxide (D-120) with styrene (St) were prepared in bulk by using benzoyl peroxide as initiator at 80°C. The compositions of the copolymers were determined by ^{1}H-NMR analysis. The reactivity ratios of D-120 and St were calculated by methods of Kelen–TüdÖs (K-T), Fineman–Ross (F-R), and Yezrielev-Brokhina-Roskin (YBR), respectively. Graft copolymers were obtained by grafting of methyl methacrylate (MMA) onto the copolymers during decomposition of peroxy bonds suspended in the backbone. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 2318–2326, 2002

Key words: graft copolymers; radical polymerization; initiators; copolymerization; NMR

INTRODUCTION

With the fast development of polymer alloys, excellent properties of multicomponent polymers such as mechanics, thermodynamics, electricity, and others require good compatibility of each component. Graft copolymer can be used as an emulsifying agent, surfactant, solubilizer, compatibilizer, phase-transfer catalyst, selective film, biomedical polymer material, thermoplastic elastomer, and so on[1–8]; consequently, studies on synthesis, characterization, and application of graft copolymers were widely carried out in recent years.[9–13]

Free-radical copolymerization to obtain graft copolymers using polyperoxide synthesized by vinyl peroxide, which have several peroxy bonds in the backbone, was developed in past years[14–15]; however, the characterization and composition of polyperoxide have not been widely reported yet. Investigation of copolymerization behavior of vinyl peroxides with vinyl monomers is of great importance to know the reactivity ratios of monomers and sequence distribution of copolymers so that the well-proportioned distribution of peroxy bonds as well as controlled grafting point in the copolymers can be achieved.

tert-Butyl-3-isopropenylcumylperoxide (commercial name D-120) is a crosslinking agent developed by Kayaku AKZO Co., which has both a double bond and a peroxy bond. As for the good heating stability of the peroxy bond (half-life time at 104°C is 10 h), the peroxy bond can be kept steady when copolymerizing with other vinyl monomers at a lower

Table I   Feed Composition and Copolymer Composition by ^{1}H-NMR Spectra

| No.	Feed Composition (molar fraction)		Time (min)	Conversion (wt %)	Area of Aromatic Protons (A$_1$)	Area of Aliphatic Protons (A$_2$)	Copolymer Composition (molar fraction)	
	D-120 (M$_1$)	St (M$_2$)					D-120 (m$_1$)	St(m$_2$)
1	0.1	0.9	30	7.2	499	397	0.055	0.945
2	0.2	0.8	45	6.3	1644	1666	0.111	0.889
3	0.4	0.6	60	8.8	1608	2379	0.238	0.762
4	0.5	0.5	90	8.5	1570	2825	0.319	0.681
5	0.6	0.4	120	3.4	1557	2991	0.360	0.640
6	0.8	0.2	150	2.5	1559	3819	0.487	0.513

temperature. So it is possible to synthesize polyperoxide via the copolymerization of D-120 with other vinyl monomers. Copolymers of D-120 can be used for preparing graft or branched polymers.

This article reports the copolymerization of D-120 with styrene and the composition of the copolymer determined by ^{1}H-NMR analysis.[16–17] The reactivity ratios of D-120 and St were calculated by the methods of Kelen–TüdÖs (K-T), Fineman–Ross (F-R), and Yezrielev-Brokhina-Roskin (YBR), respectively.[18–20] Grafting of MMA initiated by the pendent peroxy bonds on the copolymer of D120 was also explored.

EXPERIMENTAL

Materials

Styrene (St) and methyl methacrylate (MMA) (Shanghai Chemical Reagent Factory, Shanghai, China) were distilled under reduced pressure before using. Benzoyl peroxide (BPO) (Beijing Chemical Reagent Factory, Beijing, China) was recrystallized from a mixture solvent of chloroform and methanol (Shanghai Chemical Reagent Factory, Shanghai, China) (40 : 100 by volume) and then dried in a vacuum desiccator at room temperature. D-120 was supplied by Kayaku
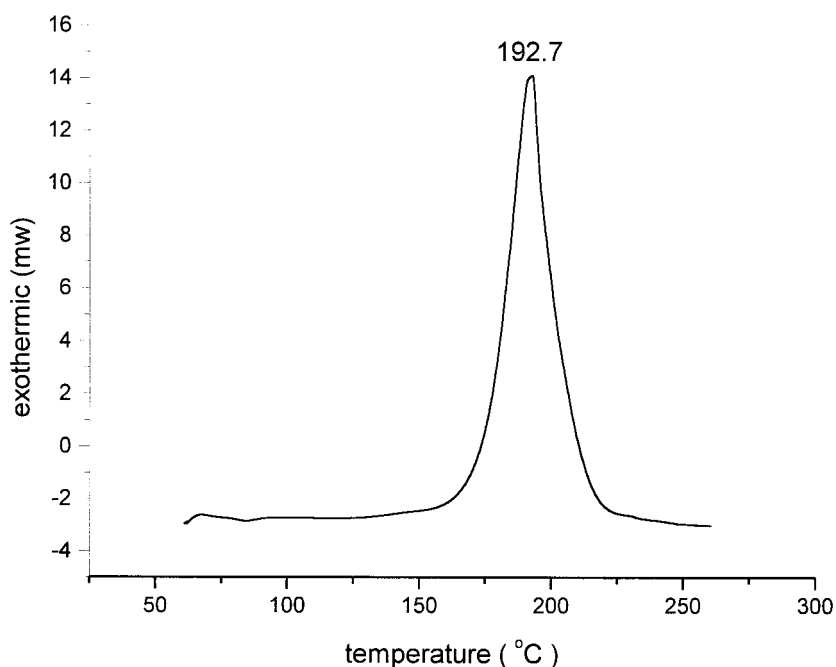
Figure 1 DSC curve of copolymers with 60% of D-120 in feed (weight: 15.81 mg).
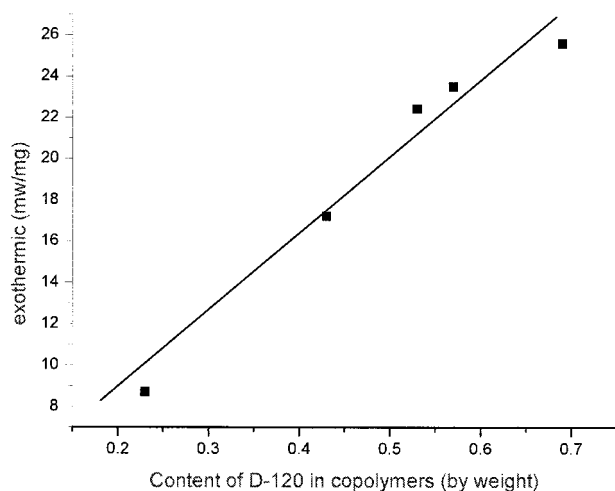
Figure 2 Curve of exothermic heat of copolymers to content of D-120 in copolymers.

AKZO Co., Japan. The oligomer and other impurities in D-120 were removed by precipitation in methanol, which was removed by distillation under reduced pressure at 28°C.

Copolymerization of D-120 and St

Appropriate quantities of St, D-120, and BPO were added to an ampoule. The mixture was flushed with oxygen-free nitrogen for 10 min. The ampoule was tightly sealed and immersed in a thermostated bath at 80°C. Copolymerization was allowed to proceed to conversion < 10%. The copolymer was precipitated in excessive methanol, filtered off, and then purified by dissolving in THF and by reprecipitating in methanol several times. The purified products were finally dried at room temperature in vacuum until constant weight. All copolymerization of St and D-120 with different initiatory feed ratios (see Table I) were performed in the same way.

Grafting MMA on the Copolymers of D-120 and St

The copolymers of D-120 and St, MMA, and solvent xylene were added to the ampoule, respectively. The feed proportion of copolymers and St was 1 : 2 by weight. The concentration of the solution was kept 40% (by weight of copolymers and graft monomer). The solution was flushed with oxygen-free nitrogen for 10 min and then tightly sealed. Grafting copolymerization was conducted at 120°C for 6 h. The product was precipitated in excessive methanol and filtered and then dried at room temperature in the vacuum until constant weight. The unreacted copolymer and homopolymer

of poly(methyl methacrylate) (PMMA) were removed by cyclohexane and acetonitrile, respectively.

Instruments

Copolymers of D-120 with St were characterized by using IR spectra, ^{1}H-NMR, GPC, and DSC, respectively. Graft copolymers were characterized by using IR spectra and ^{1}H-NMR. IR spectra were recorded with a Nicolet Magna-550 FITR spectrometer. DSC measurements were performed on a Natzsch DSC-200 instrument with a heating rate of 10°C/min. ^{1}H-NMR spectra were scanned with a Bruker MSL-300 NMR spectrometer with tetramethylsilane as internal standard and CDCl$_3$ as solvent. The molecular weight and molecular weight distribution were measured on HP 1100 GPC instrument by using THF as elute with a flow rate of 1.0 mL/min.

RESULTS AND DISCUSSION

DSC Curve of Copolymers

D-120 is a crosslinking agent developed by Kayaku AKZO Co., which has both a double bond and a peroxy bond. Similar to α-methylstyrene, D-120 could hardly polymerize at high temperature, but could copolymerize with vinyl monomers at appropriate temperatures. Figure 1 shows the DSC curve of the copolymers, where the exothermic peak around 192°C corresponds to the characteristic decomposition of peroxy groups in the copolymers. This means that the peroxy group of D-120 survived during copolymerization. The plot of exothermic heat against the molar percentage of D-120 in copolymer, calculated from the results of ^{1}H-NMR, is almost linear (from Fig. 2). It is estimated from the activity energy of decomposition (128.33 KJ/mol) and the half-time at 80°C (162 h) that only 0.1% peroxy groups of D-120 would decompose in 0.5 h. Therefore, the decomposition of
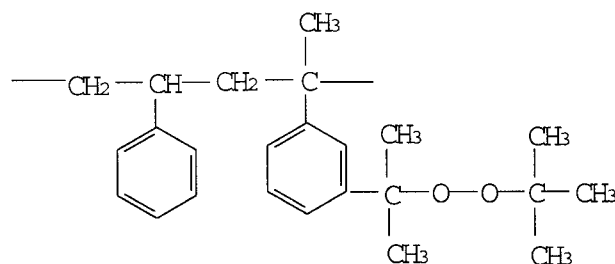
Scheme 1 Constituent monomeric units of the copolymer.
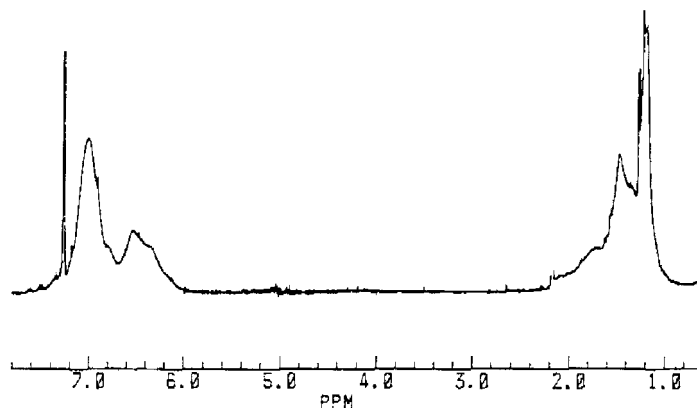
Figure 3 ^{1}H-NMR spectrum of copolymers with 40/60 of D-120/St in feed by weight.

D-120 during copolymerization in the paper is negligible, because the experiments were finished within 2 h at 80°C.

^{1}H-NMR Analysis and Composition of Copolymers

The constituent monomeric units of the copolymer can be represented as shown in Scheme 1.

Figure 3 shows the ^{1}H-NMR spectrum of one copolymer. The peak assignments are as follows: $\delta = 6.3$–7.2 (m, protons of benzene ring), 0.6–4.0 (m, protons of aliphatic chains). This shows that both the monomer units of D-120 and St can be found in the samples.

The content of each monomer in copolymers was estimated by the ^{1}H-NMR spectra. The composition of the copolymer can be calculated as follows:

Area of aromatic protons

(A_1)/Area of aliphatic protons

$$(A_2) = (4m_1 + 5m_2)/(20m_1 + 3m_1) \quad (1)$$

$$m_1 + m_2 = 1 \quad (2)$$

where m_1 and m_2 are the molar fractions of D-120 and St in copolymer, respectively. Equation (1) is based on the fact that D-120 contains 24 protons, of which 4 are aromatic and 20 are aliphatic protons, whereas St contains 5 aromatic protons and 3 aliphatic protons, respectively. Therefore, the percentage of D-120 (M) in copolymers can be calculated by:

$$m_1 = (5A_2 - 3A_1)/(17A_1 + A_2) \quad (3)$$

According to eq. (3), the compositions of copolymers were calculated and are listed in Table I. From Table I, it can be seen that with the increasing ratio of D-120 to St in feed, the ratio of them in copolymers also increased. Furthermore, the ratio in copolymer is lower than that in feed.

Molecular Weight of Copolymers

Table II shows the data of GPC for the copolymers. With the content of D-120 in copolymers increasing, M_n and M_w decrease, as well as the polydisperse coefficient (D). This indicates that

Table II   GPC Data of Copolymers with Different D-120 Content

No.	Percentage of D-120 in Copolymers (mol %)	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	D
1	5.5	29.72	47.10	1.59
2	11.1	22.99	41.57	1.89
3	23.8	10.92	18.79	1.72
4	31.9	8.92	14.27	1.60
5	36.0	7.93	13.55	1.71
6	48.7	4.84	6.24	1.29
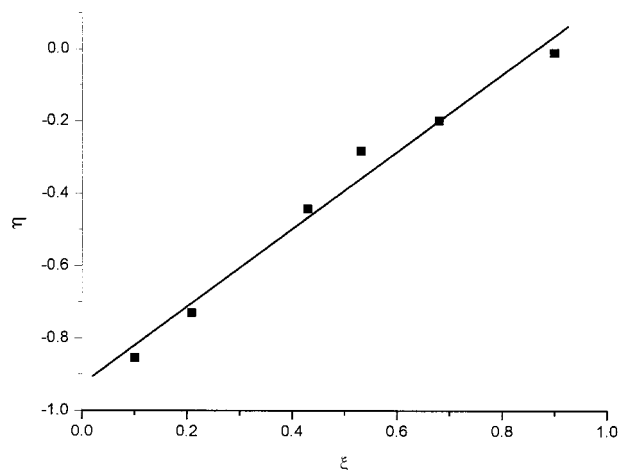
Figure 4 K-T method plot for determination of the monomer reactivity ratios of D-120 and styrene (α = 1.89).

D-120 can affect the average molecular weight and even molecular weight distribution.
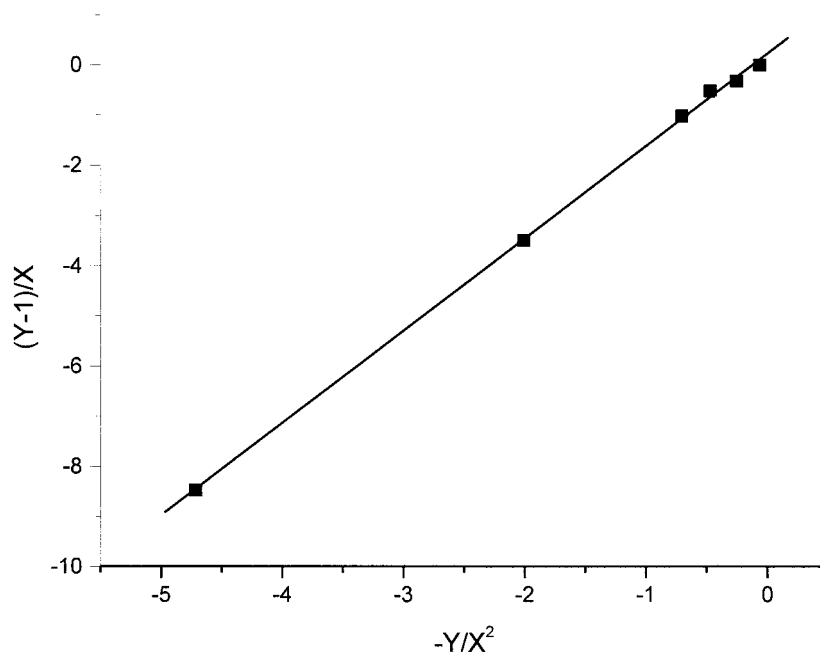
Reactivity Ratio of Copolymer

Based on the data of Table I, the reactivity ratios of D-120 and St were calculated by using the method of K-T (see Fig. 4), F-R (see Fig. 5), and YBR, respectively. The results are listed in Table III. It can be seen that these results are very close

**Table III Reactivity Ratios of D-120 and Styrene Determined by Three Methods**

Method	r_1	r_2	$r_1 \times r_2$
Kelen–TüdÖs	0.174	1.772	0.309
Fineman–Ross	0.154	1.825	0.280
YBR	0.125	1.780	0.223

to each other. The product of the reactivity ratio ($r_1 r_2$) is < 1, which shows that the copolymerization is apt to form random copolymers. Figure 6 shows the composition curves of copolymers. The curve calculated from the values of r_1 = 0.174 and r_2 = 1.772 coincides with the experimental data quite well. As the present system is reported for the first time, its reactivity ratio values could not be compared with literature values.

Investigation of copolymerization behavior of vinyl peroxides with vinyl monomers is of great importance to know the reactivity ratios of monomers as well as the sequence distribution so that the well-proportioned distribution of peroxy bonds and controlled grafting point in the copolymers can be achieved. The statistic sequence distribution of the monomers in the copolymers was calculated by the following equations[21–22]:

Figure 5 Fineman–Ross method for determination of the monomer reactivity ratios of D-120 and styrene.
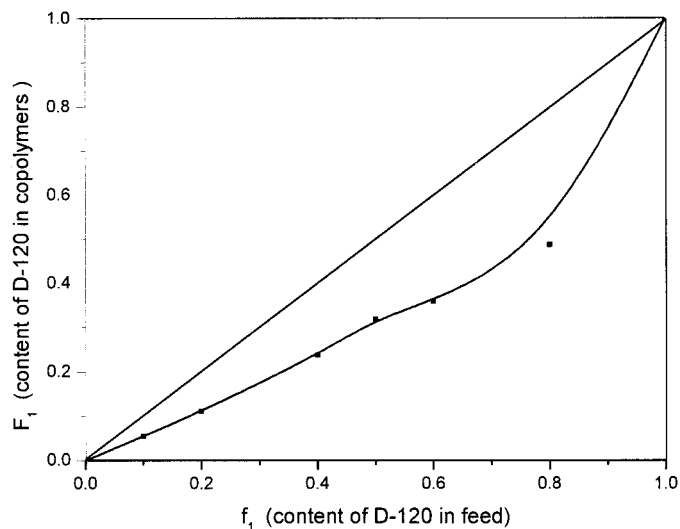
Figure 6 Monomer–copolymer composition plot of the copolymerization of D-120 with styrene (the solid line corresponds to the theoretical diagram calculated from the value of reactivity ratio by K-T method).

$$X = \phi_1 - 2\phi_1 (1 - \phi_1)/$$

$$\{1 + [(2\phi_1 - 1)^2 + 4r_1r_2\phi_1 (1 - \phi_1)]^{1/2}\} \quad (4)$$

$$Y = (1 - \phi_1) - 2\phi_1 (1 - \phi_1)/$$

$$\{1 + [(2\phi_1 - 1)^2 + 4r_1r_2\phi_1 (1 - \phi_1)]^{1/2}\} \quad (5)$$

$$Z = 4\phi_1 (1 - \phi_1)/$$

$$\{1 + [(2\phi_1 - 1)^2 + 4r_1r_2\phi_1(1 - \phi_1)]^{1/2}\} \quad (6)$$

where r_1 and r_2 are the reactivity ratios of D-120 and St, respectively, ϕ_1 is the mole percentage of D-120 in copolymer, X, Y, and Z are the sequence mole percentage of D-120-D-120, St-St, and D-120-St in copolymer, respectively. The mean sequence lengths of D-120 and St were given by

$$L_{\text{D-120}} = 1 + r_1[\text{D-120}]/[\text{St}] \quad (7)$$

$$L_{\text{St}} = 1 + r_2[\text{St}]/[\text{D-120}] \quad (8)$$

According to the reactivity ratios of $r_1 = 0.174$, $r_2 = 1.772$ (by K-T), the sequence distributions and mean sequence lengths of copolymers with different compositions were listed in Table IV, where the copolymer composition is calculated from r_1, r_2, and the monomer composition in feed. It can be seen from Table IV that when the content of D-120 in feed is small, the D-120-D-120 sequence in copolymers is also very small. With increasing the content of D-120 in feed, the D-120-D-120 sequence increases slowly and St-St sequence in copolymer decreases quickly. The D-120-St sequence

**Table IV   Sequence Distribution of Copolymers of D-120 with Styrene**

Content of D-120 (mol %)		Sequence Distribution (mol %)			Mean Sequence Length	
In Feed	In Copolymers	D-120-D-120	St-St	D-120-St	$m_{\text{D-120}}$	m_{St}
10	5.50	0.10	89.10	10.80	1.02	16.95
20	11.14	0.44	78.16	21.40	1.04	8.09
40	23.80	2.54	54.94	42.52	1.12	3.66
50	31.90	5.28	41.48	53.24	1.17	2.77
60	35.96	7.23	35.31	57.46	1.26	2.18
80	48.71	16.61	19.19	64.20	1.70	1.44
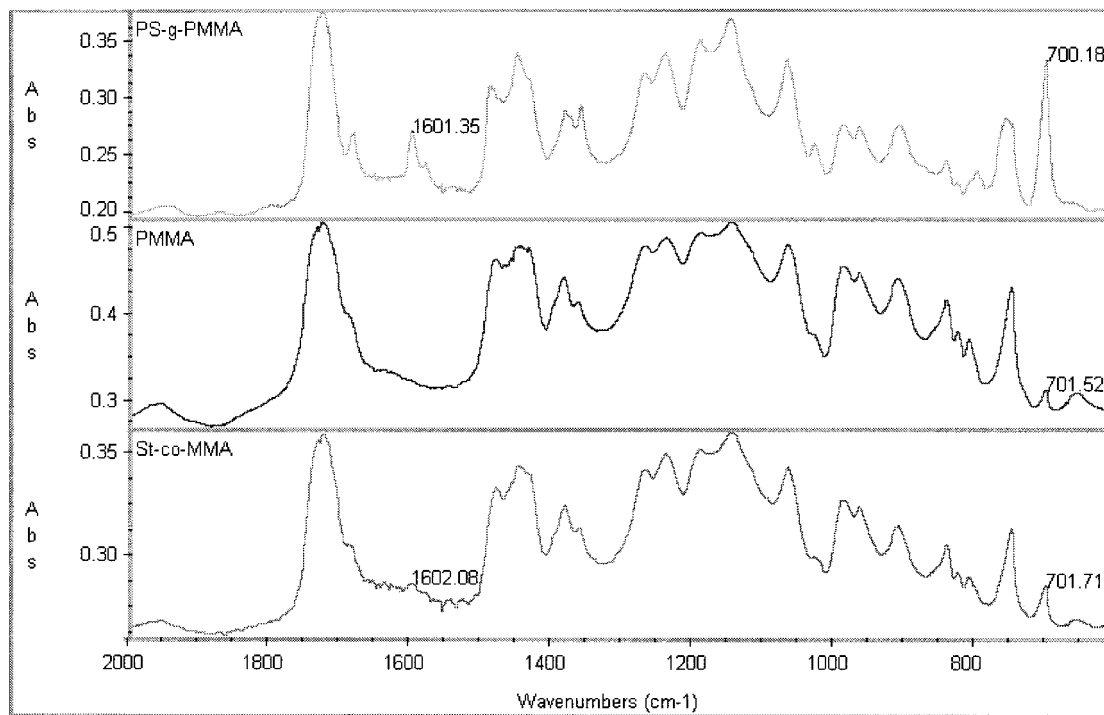
Figure 7 IR spectra of graft copolymers before and after separation from homopolymer. PS-*g*-PMMA: graft copolymer after separation; PMMA: homopolymers in the filtrate; St-*co*-MMA: before separation.

increases steadily. Obviously, the sequence distribution obtained above is an instantaneous distribution at the beginning of copolymerization; however, the real sequence distribution in the samples is close to the calculated one because of

the very low conversions. As listed in Table IV, the mole fractions of D-120-St sequences are far more than the mole fractions of D-120-D-120 sequences, which indicates that ∼ D-120 · (a polymer chain ending in a radical derived from mono-
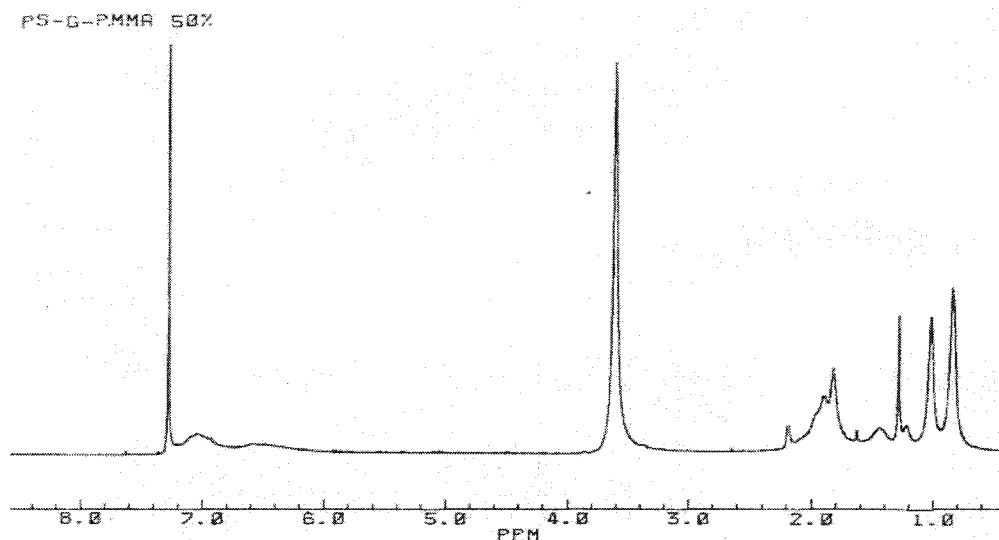
Figure 8 ¹H-NMR spectra of graft copolymers of PS-*g*-PMMA (50% of D-120 in feed).

Table V   Graft Efficiency and Graft Ratio of Graft Copolymers

No.	Content of D-120 in Backbone Copolymer (mol %)	Conversion of MMA (mol %)	Graft Ratio (wt %)	Graft Efficiency (mol %)
2	11.1	72.6	79.8	7.2
3	23.8	68.9	116.9	10.8
4	31.9	65.4	133.5	10.9
5	36.0	55.6	143.5	10.3
6	48.7	75.0	189.2	9.5

mer D-120) tends to add St remarkably in preference to D120. These data are helpful in designing the distribution of peroxy bonds on the molecules of the copolymer and distribution of grafting points during graft copolymerization.

The molecular structure of D-120 is similar to that of α-methylstyrene; the allylic inhibition and ceiling temperature of α-methylstyrene are open questions. The temperature of copolymerization in this work is higher than the ceiling temperature of α-methylstyrene. The behavior of polymerization of D120 seems to be a little different from α-methylstyrene. The difference is probably attributed to the *meta*-substituting group on the ring. Further investigation should be developed.

Characterization of Graft Copolymers

Acetonitrile was usually used to separate the mixture of PMMA and polystyrene, because homopolymer of MMA can be dissolved in acetonitrile, whereas polystyrene could not.[14] Figure 7 is the IR spectra of graft copolymers before and after separation from homopolymer of MMA. The IR spectra of separated graft copolymer which shows the absorb peak of carbonyl group proved the successful graft copolymerization of MMA onto the backbone.

Figure 8 shows ^{1}H-NMR as of one of the purified graft copolymers; all the chemical shift peaks are assigned as follows: $\delta = 0.7–2.7$ (m, —CH$_3$, —CH$_2$—, —CH—), $\delta = 3.4–3.8$ (s, —OCH$_3$, —OCH$_2$—),$\delta = 6.0–7.2$ (m, AR—H). The graft ratio and graft efficiency can be calculated by ^{1}H-NMR of graft copolymers. The results are listed in Table V. It can be seen that by increasing the D-120 content in the backbone copolymers, the graft ratio increases and the graft efficiency is almost unaffected, which implies that graft point increases and graft length decreases.

CONCLUSION

D-120 can copolymerize with St by radical reaction. The reactivity ratios of D-120 and St obtained by the method of Kelen-TüdÖs are 0.174 and 1.772, respectively. The values calculated by methods of Fineman–Ross and YBR are very close to them. Graft copolymers were obtained by grafting of MMA onto the backbones. The content of D-120 in the copolymers affects the grafting ratio.

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