Copolymerization of tert-Butyl 3-Isopropenylcumyl Peroxide with Butyl Acrylate and Grafting of Styrene onto the Copolymers

Zhiang Li, Qiangguo Du, Yuliang Yang, Mingde Lin

1 Department of Macromolecular Science, Fudan University, the Key Laboratory of Molecular Engineering of Polymers, Shanghai 200433, Peoples Republic of China
2 Department of Material Engineering, Jiangsu Institute of Petrochemical Technology, Changzhou, 213016, Peoples Republic of China
Fax: +86(21)65640293; E-mail: qgdu@fudan.edu.cn

Introduction
Graft copolymers are one of the earliest polymer alloys to be investigated and required in various fields of industrial application.\(^1\)\(^-\)\(^3\) The grafting of polystyrene or copolymer of styrene and acrylonitrile onto the polybutadiene in high-impact polystyrene and acrylonitrile–butadiene–styrene copolymer make it possible to combine rubber and plastic phases. Amphiphilic graft copolymers have been widely used as emulsifying agents, surfactants, solubilizers, compatibilizers, and phase transfer catalysts.\(^3\)\(^-\)\(^6\) Graft copolymers, in which there is microphase separation between branch and main chains, can be used for surface improvements, modifications, selective films, and biomedical polymer materials.\(^7\)\(^-\)\(^8\) In addition, they have also been incorporated into thermoplastic elastomers and plastics,\(^9\) anhydrous emulsion coating,\(^10\) and so on.

The main methods to obtain graft copolymers are classified as follows: (1) Grafting of monomers onto main chains, including radical grafting,\(^11\) anionic grafting,\(^12\) and cationic grafting;\(^13\) (2) Grafting of prepolymer onto another prepolymer;\(^14\) (3) Graft copolymerization with a macronomer, which includes radical copolymerization,\(^15\) ionic copolymerization,\(^16\) coordination copolymerization,\(^1\) group-transfer polymerization,\(^17\) and step copolymerization.\(^18\) Recently, studies of living radical copolymerization were also carried out in the preparation of a graft copolymer.\(^19\) By this means, a copolymer with a well-controlled molecular weight and molecular weight distribution, and a definite graft structure is obtained. Furthermore, the grafting efficiency is much higher.

Radical polymerization processes to obtain graft or block copolymers using polymeric peroxides as initiators, which have several O–O bonds in the macromolecule, were studied in recent years.\(^20\) Polymeric peroxides are of two main types, one of which are vinyl polymeric peroxides.
monomers; the others being acid polyperoxides, obtained by the condensation of organic dibasic acids with sodium peroxide. Vinyl polyperoxides are of interest due to their potential applications. Studies on graft or block copolymerization of polymeric peroxides, such as poly(α-methylstyrene peroxide), poly(styrene peroxide), and poly(methyl methacrylate peroxide) with monomers have been carried out.

The preparation of polyperoxide using vinyl peroxide have also been investigated recently, while the investigation of copolymerization behavior of vinyl peroxides with vinyl monomers has not been reported. It is of great importance to know the reactivity ratios of monomers and sequence distribution of copolymers so that a well-proportioned distribution of peroxy bonds as well as controlled grafting point in the copolymers can be acquired.

tert-Butyl 3-isopropenylcumyl peroxide is a commercially available crosslinking agent, D-120, developed by Kayaku AKZO Company, which contains both a double bond and a peroxy bond. As a result of the heating stability of the peroxy bond (half-life at 104 °C is 10 h), the peroxy bond can be kept stable when copolymerizing with other vinyl monomers at lower temperature. So it is possible and useful to study the copolymerization of D-120 with other vinyl monomers. The present paper reports the copolymerization of D-120 with BA and grafting of styrene onto the copolymers.

**Experimental Part**

**Materials**

BA and styrene (St) (Shanghai Gaoqiao Petrochemical Co.) were distilled under reduced pressure prior to use. Benzoyl peroxide (BPO) (Beijing Chemical Reagent Factory) was recrystallized twice from a mixture of chloroform and methanol (40:100 by volume) and dried under vacuum. D-120 was supplied by Kayaku AKZO Co (Japan). The oligomer and other impurities in D-120 were removed by precipitation in methanol, which was subsequently removed by distillation under reduced pressure at 28 °C.

**Copolymerization of D-120 with BA (see Scheme 1)**

Appropriate quantities of BA, D-120 and BPO were added to an ampoule respectively. The mixture was flushed with oxygen-free nitrogen for at least 10 min. The ampoule was tightly sealed and immersed in a bath equipped with a thermostat at 80 °C. Copolymerization was allowed to proceed to conversion of less than 10%. The copolymer was precipitated in excessive methanol, filtered off, and then purified by dissolving in tetrahydrofuran (THF) and reprecipitating in methanol several times. The purified products were finally dried at room temperature under vacuum until constant weight was recorded. All copolymers of BA and D-120 with different initiatory compositions (see Table 1) were prepared using the same procedure. Copolymers were characterized by infrared (IR) spectroscopy, ^1^H NMR, differential scanning calorimetry (DSC) and gel permeation chromatography (GPC) analyses.

**Grafting Styrene onto the Copolymers of D-120 with BA (see Scheme 2)**

A copolymer of D-120 with BA, St, and xylene were added to an ampoule. The feed proportion of copolymers and St was 1:2 by weight. The concentration of the solution was kept at 40% (by the weight of copolymers and the monomer). The solution was flushed with oxygen-free nitrogen for 10 min and then tightly sealed. Grafting copolymerization was conducted at 120 °C for 3 h. The product was precipitated in excessive methanol and filtered, and finally dried at room temperature under vacuum until constant weight was recorded.

**Separation of Graft Copolymers from Homopolymers after Saponification**

Graft copolymers and homopolymers products of the grafting reaction were separated by saponification at room temperature. The sample (0.5 g) was dissolved in 30 ml of solvent – a mixture of THF and methanol (2:1 by volume) – and 10 ml of 1-M NaOH/methanol was added to the solution.
The saponification was performed for 22 h at 30 °C with constant stirring. The precipitant was dried under vacuum after filtration and characterized by 1H NMR analysis.

**Instruments**

IR spectra were recorded with a Nicolet Magna-550 FT-IR spectrometer. DSC measurements were performed on a Netzsch DSC-200 instrument at a heating rate of 10 °C min⁻¹. 1H NMR spectra were scanned with a Bruker MSL-300 NMR spectrometer with tetramethylsilane as the internal standard and CDCl₃ as the solvent. The molecular weight and molecular weight distribution were measured on an HP 1100 instrument using THF as the eluent and a flow rate of 1.0 mL min⁻¹.

**Results and Discussion**

**Solubility of Copolymers**

Similarly to α-methylstyrene, only oligomers can be obtained by the homopolymerization of D-120. However, copolymerization of D-120 with other vinyl monomers such as BA is possible. The copolymer of D-120 with BA is soluble in THF, chloroform, N,N-dimethylformamide, dimethyl sulfoxide, toluene, dimethyl benzene, and benzene, but insoluble in methanol, ethanol, hexane, liquid paraffin, and water.

**1H NMR Spectra and Composition of Copolymers**

Figure 1 shows the 1H NMR spectrum of one of the copolymers. The peak assignments are as follows: δ = 6.3–7.2 (m, protons of benzene ring), 0.6–4.0 (m, protons of aliphatic chains). This shows that monomer units of both D-120 and BA can be found in the samples.

The content of each monomer in copolymers was estimated by the 1H NMR Spectra. The composition of the copolymer can be calculated from:

\[
\text{area of aromatic protons } (A_1) = \frac{4m_1}{20m_1 + 12m_2}
\]

\[
m_1 + m_2 = 1
\]

where \(m_1\) and \(m_2\) are the molar fraction of D-120 and BA in copolymer, respectively. Thus the \(m_1\) can be calculated as follows:

\[
m_1 = \frac{3A_1}{A_2 - 2A_1}
\]

According to Eq. (3), the compositions of copolymers were calculated and listed in Table 1. From Table 1, it can be seen that with increasing D-120 in the feed, the content of D-120 in the copolymer also increased. Furthermore, the ratio of the two monomers in copolymer is higher than that in the feed.

**IR Spectra of Copolymers**

Figure 2a shows the IR spectra of D-120 after purification. Figure 2b represents copolymers with different composition of D-120 and BA. The main absorption peaks of copolymer are assigned as: 1731 cm⁻¹ (\(-\text{CO}–\)), 1601 cm⁻¹ (benzene ring), 875 cm⁻¹ (\(-\text{O–O}–\)); 1162 cm⁻¹ (\(-\text{C–O–C}–\)). This proved the existence of D-120 units in the copolymer. From the IR spectra it can be observed that with increasing D-120 in the feed, the height ratio of the absorption peak at 875 cm⁻¹ to that at 1162 cm⁻¹ increases gradually. Figure 3 is the plot of the height ratio of IR absorption against the composition ratio of the copolymer calculated above from the 1H NMR. The linearity of the curve shows that both results are coincident.

<table>
<thead>
<tr>
<th>No.</th>
<th>D-120 in feed mol-%</th>
<th>BA in feed mol</th>
<th>Content of D-120 in copolymer mol-%</th>
<th>Reaction time min</th>
<th>Conversion wt-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>0.018</td>
<td>28.28</td>
<td>30</td>
<td>7.17</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>0.016</td>
<td>41.93</td>
<td>45</td>
<td>6.25</td>
</tr>
<tr>
<td>3</td>
<td>35</td>
<td>0.013</td>
<td>55.65</td>
<td>60</td>
<td>8.78</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>0.010</td>
<td>62.88</td>
<td>90</td>
<td>8.50</td>
</tr>
<tr>
<td>5</td>
<td>65</td>
<td>0.007</td>
<td>70.16</td>
<td>120</td>
<td>2.25</td>
</tr>
</tbody>
</table>
Copolymerization of tert-Butyl 3-Isopropenylcumyl Peroxide...

DSC Curves of Copolymers

Figure 4 shows the DSC curves 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 mole percent of D-120 in the copolymer, calculated from the results of 1H NMR, is almost linear (Figure 5). This shows again that both the results of DSC and the results of 1H NMR are coincident.

Kayaku AKZO Co. reported in the production specification that the half-lives at 104°C, 126°C, and 152°C are 10 h, 1.0 h, and 0.1 h, respectively. It can be estimated that only about 0.1% of the peroxy groups of D-120 would decompose at 80°C in 0.5 h. Therefore the decomposition of D-120 during the copolymerization carried out by us negligible, because the experiments were finished within 2 h and at 80°C.

GPC of Copolymers

Table 2 shows the GPC data for the copolymers. As the content of D-120 in the copolymers increase, $M_n$, $M_w$, and $M_z$ decrease, as does the polydispersion coefficient ($D$). This shows that D-120 can affect the average molecular weight and even the molecular weight distribution.

Reactivity Ratio and Sequence Distribution of Copolymer of D-120 with BA

In this work three methods to determine the reactivity ratio are used, which are $K$–$T$, $F$–$R$ and $YBR$ according to the equations below:

![Figure 2. (a) IR spectra of D-120; (b) IR spectra of copolymers of D-120 with BA. Percentage of D-120 in the feed: (1) 10%; (2) 20%; (3) 35%; (4) 50%; (5) 65.]

![Figure 3. Calibration curve of the IR spectra of the copolymer.]

![Figure 4. DSC curves of copolymers. Percentage of D-120 in the feed: (B) 50%; (D) 65%; (F) 10%; (H) 20%; (J) 35%.]

![Figure 5. The relationship between the exothermic heat and the molar percent of D-120 in copolymers.]
Table 2. GPC data.

<table>
<thead>
<tr>
<th>No.</th>
<th>Percent of D-120 in feed</th>
<th>$M_n \times 10^4$</th>
<th>$M_w \times 10^4$</th>
<th>$M_z \times 10^4$</th>
<th>$D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>3.17</td>
<td>5.83</td>
<td>10.16</td>
<td>1.84</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>1.71</td>
<td>2.47</td>
<td>3.49</td>
<td>1.44</td>
</tr>
<tr>
<td>3</td>
<td>35</td>
<td>1.54</td>
<td>2.16</td>
<td>3.05</td>
<td>1.40</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>1.31</td>
<td>1.66</td>
<td>2.10</td>
<td>1.27</td>
</tr>
<tr>
<td>5</td>
<td>65</td>
<td>1.00</td>
<td>1.45</td>
<td>1.98</td>
<td>1.45</td>
</tr>
</tbody>
</table>

where $\eta = X(Y-1)/(aY + X^2), \xi = X^2/aY + X^2, a = [(X^2/Y) \text{min} (X^2/Y) \text{max}]^{1/2}, X = [M_1/M_2]$ (molar ratio in feed), $Y = d[M_1/d[M_2]$ (molar ratio in copolymers); $A_1 = \Sigma (X/Y), A_2 = \Sigma (Y/X), C_1 = \Sigma X(1-1/Y), C_2 = \Sigma (Y/X)(1/Y-1), n$ is the number of experimental; while $\xi^2 = \Sigma n^2/n-2, \xi^2 = [(X/Y)^{1/2}r_1 - (Y/X)r_2 + (1/Y)^{1/2} - Y^{1/2}]^{1/2}$.

Based on the data of Table 1, the reactivity ratios of D-120 and BA were calculated using the methods of K-T (see Figure 6), F-R (see Figure 7a and 7b, where the final result of $r_1$ and $r_2$ is the average value from Figure 7a and 7b), and YBR. The results are listed in Table 3. It can be seen that these results are in accordance with each other. The product of reactivity ratio $(r_1 r_2)$ is less than 1, which means that the copolymerization tends to form random copolymers. Figure 8 is the composition curves of copolymers. The curves calculated from the values of $r_1 = 1$ and $r_2 = 0.2$ coincide with the experimental data quite well. From Figure 8, it is found that with increasing D-120 in the feed, the percent of D-120 in the copolymer increases faster at first and then slower. According to the Alfrey and Price $Q$ and $e$ equation $[Q = (Q_0/r_1) \exp(-\epsilon_1(e_1-e_2))$ and the values of $Q (0.5)$ and $e (1.06)$ for BA, the values of $Q$ and $e$ for D-120 was calculated and listed in Table 3. The greater value of $Q$ for D-120 compared to that of BA indicates that D-120 can easily induce free radical formation. The negative value of $e$ indicates to ability to provide an electron and as these values of the two monomers are close to each other, they can copolymerize easily.

In order to show this character more clearly, the statistic sequence distribution of the monomers in the copolymers was calculated using the following equations.\[32]
Copolymerization of tert-Butyl 3-Isopropenylcumyl Peroxide ...

\[ X = \frac{\Phi_1 - 2\Phi_1 (1 - \Phi_1) / [1 + (2\Phi_1 - 1)^2]}{1 + (2\Phi_1 - 1)^2} \]

\[ Y = \frac{1 - \Phi_2 - 2\Phi_1 (1 - \Phi_1) / [1 + (2\Phi_1 - 1)^2]}{1 + (2\Phi_1 - 1)^2} \]

\[ Z = \frac{4\Phi_1 (1 - \Phi_1) / [1 + (2\Phi_1 - 1)^2] + 4 r_1 r_2 \Phi_1 (1 - \Phi_1)[1 + (2\Phi_1 - 1)^2]}{(1 - \Phi_1)[1 + (2\Phi_1 - 1)^2]} \]

where \( r_1 \) and \( r_2 \) are the reactivity ratio of D-120 and BA respectively, \( v_1 \) is the mole percent of D-120 in copolymer. \( X, Y \) and \( Z \) represent the mole percent of D-120–D120, BA–BA, D-120–BA in the copolymer, respectively. According to the reactivity ratios of \( r_1 = 0.966, r_2 = 0.178 \) (by K-T), the sequence distribution of copolymers with different composition is listed in Table 4, where the copolymer composition is calculated from \( r_1, r_2 \), and the monomer composition in the feed. It can be seen from Table 4 that the D-120–BA sequence is the main sequence. When the content of D-120 in the feed is small, the D-120–D120 sequence in copolymers is also very small. However, with increasing content of D-120 in feed, the D-120–D120 sequence increases and the BA–BA sequence in the copolymer decreases proportionally. The D-120–BA sequence increases slowly at first, is at its highest when the content of the D-120 in the feed is 35%, and then decreases slowly. 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 due to the very low conversions.

The molecular structure of D-120 is similar to that of \( a \)-methylstyrene. The allylic inhibition and ceiling temperature of \( a \)-methylstyrene are open questions. The temperature of copolymerization in this work is higher than the ceiling temperature of \( a \)-methylstyrene, however, the experimental results here show the existence of a greater number of sequences of D-120–D120. The behavior of polymerization of D-120 seems to be a little different from that of \( a \)-methylstyrene. The difference is probably attributed to the meta-substituting group on the ring. Further investigation is needed to determine this point.

**Characterization of Graft Copolymers**

After 3 h of graft copolymerization of St on the copolymer of D-120 with BA, 89% conversion of styrene was achieved. As a comparison, only 18% conversion could be obtained in the case of polybutyl acrylate as the copolymer. This shows that the peroxy groups in the copolymer of D-120 can initiate the polymerization of St.

In order to determine the graft efficiency, the homopolymer must be removed from the product of graft copoly-
merization, a process that is normally difficult to effect. We failed to find a solvent that dissolves polystyrene and that does not dissolve the graft copolymer of styrene on the backbone. Fortunately it was found that the solubility of polybutyl acrylate changed greatly after saponification, therefore, separation was possible. The extent of saponification of the graft copolymer was not measured because of the peaks in the $^1$H NMR spectra were indistinguishable, but under the same reaction conditions, the saponification of the homopolymer of butyl acrylate is completed according to $^1$H NMR analysis. Assuming all the BA units are converted during saponification, the graft ratio after separation from the homopolymer. The results listed in Table 5 indicate that St can be grafted onto the backbone using the route described in this paper.

The graft efficiency was only 32% by weight. This is because homopolymerization of styrene can be initiated by heat and by the fragmentary free radicals $^\cdot$OC(CH$_3$)$_3$, formed during decomposition of the pendent peroxy groups of the copolymer of D-120.

**Conclusion**

D-120 can copolymerize with BA. The reactivity ratios of D-120 and BA obtained by the method of K-T are 0.966 and 0.178, respectively, very close to the results calculated by the methods of F-R and YBR. The molecular weight of the copolymer decreases with an increasing content of D-120 in the feed. The pendent peroxy groups in the copolymer can initiate the graft copolymerization of St onto the copolymer D-120.

**Acknowledgement:** Special Funds for Major State Basic Research projects (G199064800) are greatly acknowledged.

---

**Table 5. The results of graft copolymerization.**

<table>
<thead>
<tr>
<th>No.</th>
<th>Backbone polymer</th>
<th>Time h</th>
<th>Temp °C</th>
<th>Conversion %</th>
<th>Graft ratio wt-%</th>
<th>Graft efficiency wt-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>PBA-co-D-120</td>
<td>3</td>
<td>120</td>
<td>89</td>
<td>57</td>
<td>32</td>
</tr>
<tr>
<td>6</td>
<td>PBA</td>
<td>3</td>
<td>120</td>
<td>18</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

---