Graft Polymerization of Styrene onto Random Ethylene–Propylene Diene Monomer

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SYNOPSIS

The graft copolymerization of styrene (St) onto random ethylene–propylene diene monomer (EPDM) with benzoyl peroxide (BPO) and 2,2-azo-bis-isobutyronitrile (AIBN) as the initiator in solvent was studied. Results showed that BPO was superior to AIBN. The influence factors, such as reaction St and BPO, on the extent of graft were discussed. The existence of a grafted copolymer was verified by infrared spectra, NMR, and thin-layer chromatography. The grafted copolymer was characterized by thermally stimulated current. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

There were three methods for graft copolymerization of monomer onto ethylene–propylene diene monomers (EPDM): (1) the olefin hydrocarbon onto peroxidating EPDM was graft-copolymerized,[1] (2) the graft copolymer was prepared by means of melt reaction of EPDM with graft-monomer and peroxide,[2] and (3) The graft copolymerization of graft monomer onto EPDM was carried out in solvent using peroxide as the initiator.[3] The graft copolymerization of styrene (ST) onto EPDM was studied by different methods,[4-10] but the graft-copolymer of high molecular weight could not be obtained. In this article, the aim of our study was to elucidate the influences of the reaction parameter on grafting styrene (St) onto EPDM using benzoyl peroxide (BPO) as initiator in xylene medium and to determine the existence of graft-copolymer (EPDM-g-St) with infrared spectroscopy (IR), NMR, and thin-layer chromatography (TLC). EPDM-g-St was characterized by thermally stimulated current (TSC).

EXPERIMENTAL

Materials

Random EPDM (Mooney viscosity 45, the ratio of ethylene with propylene was 2 : 1, the content of dicyclopentadiene is equal to 0.1%) from Lanzhou Petrochemical Company (Lanzhou, China) was used after it was extracted by acetone and dried. Polystyrene (PS) used in this work was amorphous polymer with molecular weight $(\bar{M}_w) \sim 1.6 \times 10^5$, produced by Yanshan Petrochemical Company (Beijing, China). St, BPO, and 2,2-azo-bis-isobutyromitrile (AIBN) and other chemicals [potassium iodie (KI), iodine (I), anhydride (MAH), xylene, and acetone] were dosed as received.

Synthesis

In a four-necked round bottom flask under nitrogen, the graft reaction was carried out in anhydrous xylene at 60–100°C. The product (white) was precipitated in acetone after the reaction was finished. The ungrafted St was extracted out in a Soxhlet extractor with acetone–methyl acetone mixture for 72 h and EPDM-g-St was obtained after drying.
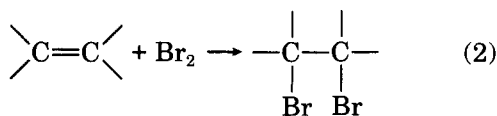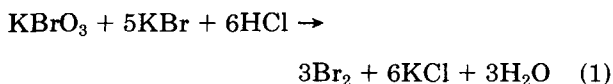
Characterization

The IR spectra of the film specimens on Necolet FT-IR 0.5 spectrometer was measured and the graft-

percent of St onto EPDM was calculated. The existence of EPDM-g-St was verified by TLC and NMR (Bruker AC-200 1H). The structure of EPDM-g-St was studied by TSC.

Analysis of double bond

In a flask, the reaction of sample with excessive $KBrO_3$–KBr solution was as follows:

$$KBrO_3 + 5KBr + 6HCl \rightarrow$$

$$3Br_2 + 6KCl + 3H_2O \quad (1)$$

$$\text{\Large $\diagdown$}C{=}C\text{\Large $\diagup$} + Br_2 \longrightarrow -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}- \quad (2)$$
$$Br \quad Br$$

After the reaction was finished, KI was put into the reaction system and I_2 was separated, which is titrated by the standard $Na_2S_2O_3$ solution. The content of double bond (E) could be calculated by the equation

$$E = \frac{(V_1 - V_2)M \times 26}{W} \times 100\% \quad (3)$$

where V_1 is the consumed volume of standard $Na_2S_2O_3$ in blank system [for eq (1)] (mL), V_2 is the consumed volume of standard $Na_2S_2O_3$ in sample system [for eqs (1) and (2)] (mL), M is the concentration of $Na_2S_2O_3$, and W is the weight of the sample.

RESULTS AND DISCUSSION

Graft Copolymerization of St onto EPDM

Figure 1 depicts the effect of the type of initiator on the extent of grafting. These results indicate that the grafting reaction of BPO was larger than with AIBN. It is similar to the grafting of MAH onto electron paramagnetic resonance[11] and PcBR.[12] The graft percent using BPO was larger than when using AIBN, which was due to the resonance stabilization of the $C{-}C^{\bullet}$ radical being above the benzoyl radical. The content of double bond (E) in pure EPDM and EPDM-g-St was measured by chemical analysis and their values are 9.3% and 9.2%, respectively. It is clear that the double bond in EPDM-g-St is not reacted. Thereby, the overall mechanism of graft polymerization of St onto EPDM is decomposition of initiator:
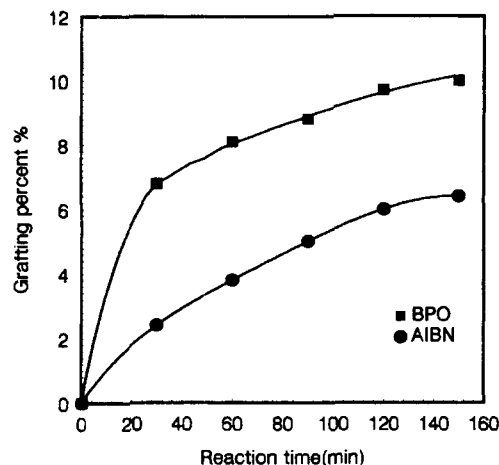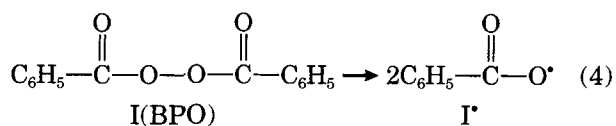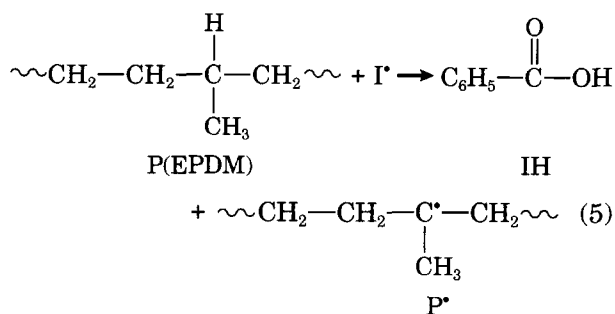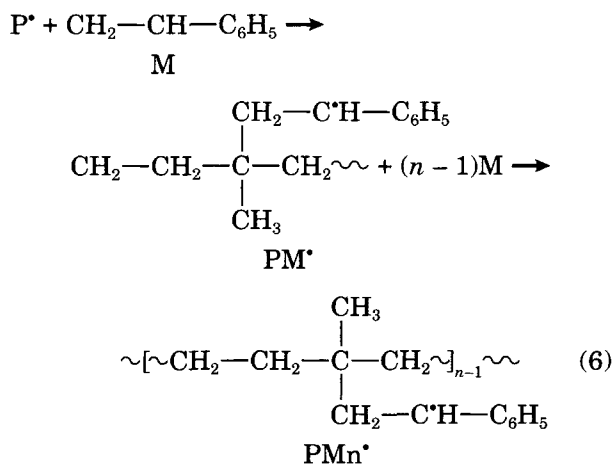

Figure 1 Influence of type of initiator. [EPDM] = 60 g/L, [St] = 0.3 mol/L, [BPO] = 1×10^{-3} mol/L, [AIBN] = 1×10^{-3} mol/L.

$$C_6H_5{-}\overset{\overset{\textstyle O}{\|}}{C}{-}O{-}O{-}\overset{\overset{\textstyle O}{\|}}{C}{-}C_6H_5 \longrightarrow 2C_6H_5{-}\overset{\overset{\textstyle O}{\|}}{C}{-}O^{\bullet} \quad (4)$$
$$I(BPO) \qquad\qquad\qquad\qquad I^{\bullet}$$

Main-chain polymer radical formation:

$$\sim\!\!\sim CH_2{-}CH_2{-}\overset{\overset{\textstyle H}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}{-}CH_2\!\!\sim\!\!\sim + I^{\bullet} \longrightarrow C_6H_5{-}\overset{\overset{\textstyle O}{\|}}{C}{-}OH$$
$$P(EPDM) \qquad\qquad\qquad\qquad IH$$

$$+ \sim\!\!\sim CH_2{-}CH_2{-}\overset{}{\underset{\underset{\textstyle CH_3}{|}}{C^{\bullet}}}{-}CH_2\!\!\sim\!\!\sim \quad (5)$$
$$P^{\bullet}$$

Formation of graft polymer radical:

$$P^{\bullet} + \underset{M}{CH_2{-}CH{-}C_6H_5} \longrightarrow$$

$$CH_2{-}CH_2{-}\overset{\overset{\textstyle CH_2{-}C^{\bullet}H{-}C_6H_5}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}{-}CH_2\!\!\sim\!\!\sim + (n-1)M \longrightarrow$$
$$PM^{\bullet}$$

$$\sim[\!\!\sim CH_2{-}CH_2{-}\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_2{-}C^{\bullet}H{-}C_6H_5}{|}}{C}}{-}CH_2\!\!\sim]_{n-1}\!\!\sim \quad (6)$$
$$PMn^{\bullet}$$
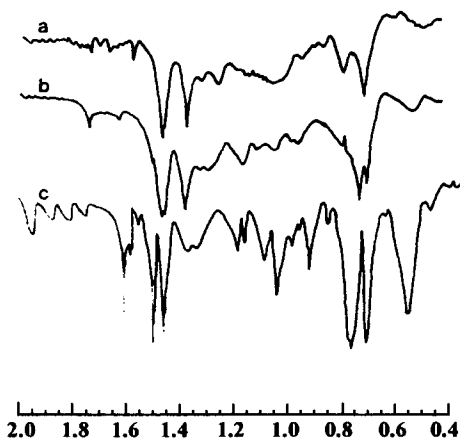
Figure 2 FT-IR spectra of EPDM, St, and EPDM-g-St (BPO initiator). (a) EPDM, (b) EPDM-g-St, (c) PS.

Figure 3 Relation of Cx/Cy with A_{700} cm^{-1}/A_{1380} cm^{-1}.

The reaction (5) was important for the formation of radical on the main chain, and reaction (6) was important for the formation of graft copolymer radical, and the graft copolymer was obtained by addition of these radicals.

Figure 2 shows the IR spectrum of EPDM, EPDM-g-St (after extracte), and PS. The IR spectrum of EPDM [Fig. 2(a)] reveals the —CH$_2$ rocking vibration at 1463.3 cm^{-1}, the —CH$_3$ symmetric bending vibration at 1376.2 cm^{-1}, and the —(CH$_2$)$_n$- wagging vibration at 722.1 cm^{-1}. Figure 2(c) shows the IR spectrum of PS; the peak at 700–900 cm^{-1} was an out-of-plane vibration of hydrogen on benzene ring, and the peak at 1450–1600 cm^{-1} was C=C plane vibration. The IR spectrum of EPDM-g-St [Fig. 2(b)] reveals the double at 700–750 cm^{-1}, which was out-of-plane of hydrogen bending vibration on benzene. The kind and amount of impurity, plasticizer, polymer blend, etc., present in a polymer can often be determined if the spectrum of the pure polymer is known and if the compound to be determined has absorption bands that are not masked by spectrum of the polymer. The grafting copolymer can also be analyzed in this fashion. The grafting percent of St onto EPDM can be determined by the ratio of the two absorption band intensities:

$$C_x/C_Y = kAx/Ay \qquad (7)$$

where C_x and C_y are the molar concentration of PS and EPDM. A is the absorbance for the corresponding wavelength. Figure 3 shows the result of C_x/C_y with A_{700} cm^{-1}/A_{1380} cm^{-1}. In this work, the grafting percent of St onto EPDM in EPDM-g-St was determined by eq. (7).

Figure 4 indicates NMR spectrum of EPDM-g-St after extract. The resonance peak of —CH$_3$ pro-
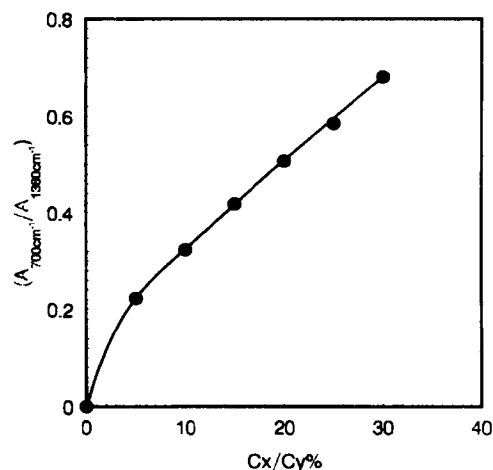
ton was at δ = 1.23 ppm in EPDM, and the resonance peak of ortho-hydrogen of styrene was at δ = 6.58 ppm. The resonance peak of meta-hydrogen and para-hydrogen proton was at δ = 7.08 ppm. Therefore, the existence of EPDM-g-St was proved by this result.

Figure 5 indicates the TLC of PS, EPDM, PS/EPDM, and PS/EPDM-g-st alloys, and the developer was an iodine-ethanol solution. The position of extension in PS/EPDM-g-st was different from PS, EPDM, and PS/EPDM. Thereby, the existence of PS/EPDM-g-st was verified.

Influence of reaction parameters

Concentration of St

Figure 6 indicates the extent of grafting increased with increasing concentration of St up to a maximum value and then decreased. Before the maximum
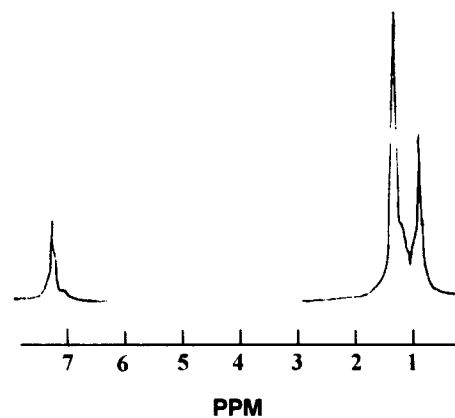

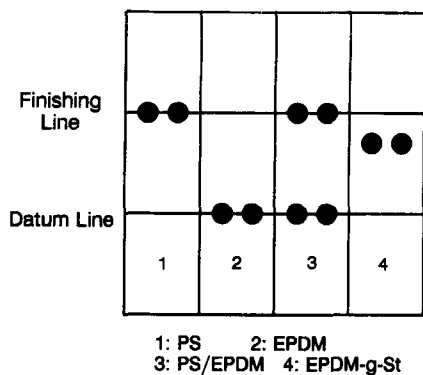**Figure 4** NMR spectra of EPDM-g-St (BPO initiator, $G\%$ = 32.6%).

1: PS   2: EPDM
3: PS/EPDM   4: EPDM-g-St

Figure 5   Result of TLC.

Figure 7   Grafting as a function of BPO concentration. [EPDM] = 60 g/L, [St] = 0.3 mol/L, 90°C, 2 h.

value, the extent of grafting increased with increasing number of monomer [reaction (6)]. When the grafting percent was over maximum value, the number of St homopolymer increased with increasing amount of monomer also and then the grafting percent decreased.

Concentration of BPO

The influence of the concentration of BPO on grafting percent was very obvious (Fig. 7). The extent of grafting increased with increasing concentration of BPO lead to a maximum value and then decreased. These results were the same as in the influence of St. At the same time, when the percent was over maximum value, the amount of monomer radical, polymer radical, and graft copolymer radical increased with increasing concentrations of BPO, which increased the probability of interaction of
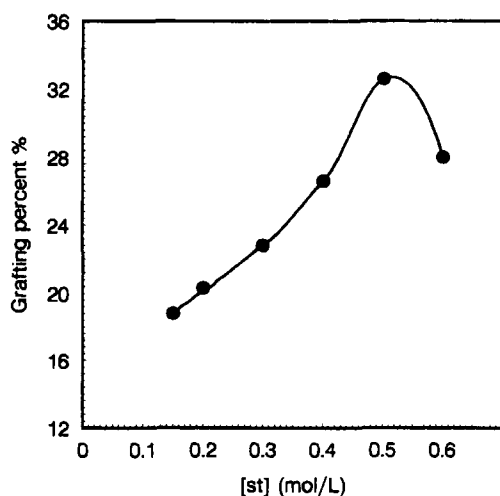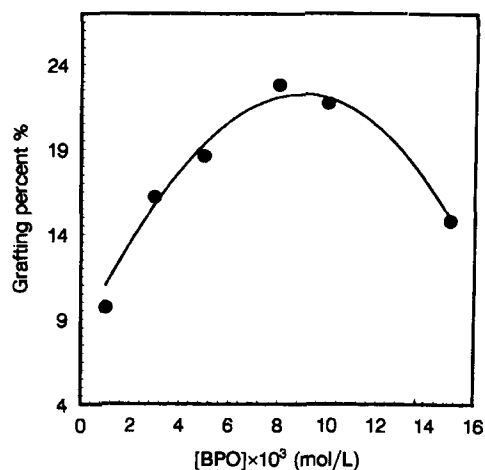
radicals and therefore, the grafting percent of St onto EPDM was decreased. The viscosity of polymerization was increased, and because of the increasing concentration of BPO that was evident, the movement of radicals was difficult.

Reaction temperature

The extent of grafting increased with increasing temperature (Fig. 8) before 90°C, presumably because of the reduction of the half-life of BPO with rising temperature, which would increase the number of $P°$ radicals [reaction (5)]. When the temperature was over 90°C, the extent of grafting decreased with rising temperature because the number of rad-
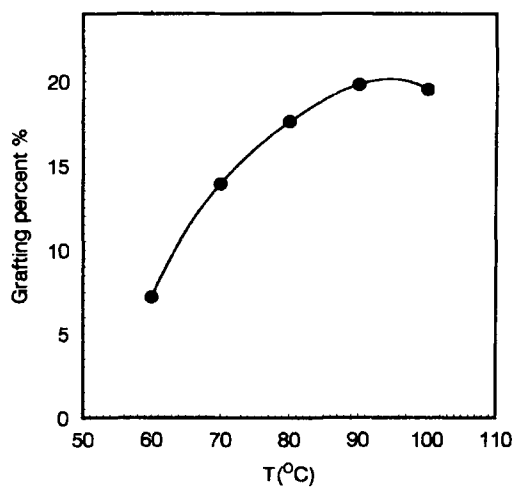

Figure 6   Grafting as a function of St concentration. [EPDM] = 60 g/L, [BPO] = 8 × 10^{-3} mol/L, T = 90°C, 2 h.

Figure 8   Grafting as a function of reaction temperature. [EPDM] = 60 g/L, [St] = 0.3 mol/L, [BPO] = 1 × 10^{-3} mol/L, 2 h.

icals was decreased with increasing velocity of decomposition on BPO.

Thermal-stimulated current

Figure 9 shows the TSC relaxational spectrums of TSC on EPDM, PS, and EPDM-g-St. There were two transition peaks in EPDM [Fig. 9(c)]. The glass transition (T_g) of EPDM was at $-52°C$, and the transition peak at $120°C$ was liquid–liquid transition (T_{ll}) of EPDM. The glass transition of PS was at $111°C$. The transition peak at $160°C$ was liquid–liquid transition (T_{ll}) of PS. (These results are identical to those of Shinichi[13] and Schmeider.[14]) The glass transition of a part of EPDM in EPDM-g-st was at $-23°C$ $(G = 32.6\%)$ [Fig. 9(a)]. The transition peak at $120°C$ may include the two peaks, which were T_{ll} transition of EPDM and T_g transition of a part of PS in EPSM-g-st. Table I shows that the glass transition temperature (T_g) of the rubber phase in EPDM-g-st rose with increasing grafting percent of grafting St onto EPDM. These results revealed the existence of EPDM-g-st, and the grafting percent affects molecular motion of EPDM with grafting percent of grafting PS onto EPDM.

Conclusions

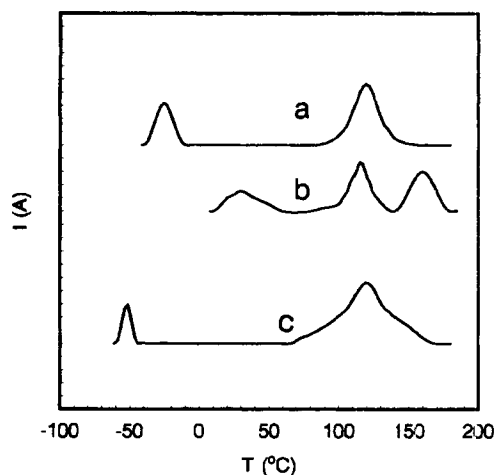Compared with AIBN, BPO is a better initiator for grafting St onto random EPDM. The maximum

Figure 9   TSC spectra of EPDM, St, and EPDM-g-St (grafting percent 32.6%). (a) EPDM-g-St, (b) PSt, (c) EPDM.

Table I   The Relation of Grafting Percent to T_g of PS Phase

Grafting Percent	0	22.8	28	32.6
T_g (°C)	-52	-30	-25	-23

grafting percent is 32.6%, depending on the reaction parameters. The double bond in EPDM-g-st was not reacted by chemical analysis. The existence of a grafting copolymer (EPDM-g-st) was proved, and the characterization of the grafting copolymer was shown by IR, NMR, TLC and TSC. The T_g of a part of EPDM in EPDM-g-St rose as the grafting percent of grafting St onto EPDM was increased.

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