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INVESTIGATION OF GRAFT POLYMERIZATION OF MALEIC ANHYDRIDE ONTO POLYBUTADIENE RUBBER

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ABSTRACT

Maleic anhydride (MAH) was grafted onto poly-*cis*-butadiene rubber (PcBR). Results showed that BPO was superior to AIBN as an initiator, and oxygen had an inhibiting effect on the reaction. The influence of factors, such as the reaction temperature and the concentrations of MAH and BPO, on the extent of grafting were studied. The polymer–probe interaction parameter (χ_{12}) and the solubility parameter (δ_2) of PcBR-*g*-MAH were estimated via inverse gas chromatography with the probe molecules $n\text{-}C_nH_{2n+2}$, $n = 6\text{–}10$. The data revealed that grafting MAH increases the polarity of PcBR and reduces its contact angle against water.

INTRODUCTION

The nonpolar poly-*cis*-butadiene rubber (PcBr) can be modified by grafting monomers, such as methyl methacrylate, styrene, vinyl acetate, and acrylamide [1-5], onto its backbone. Only a few papers dealing with PcBR MAH (maleic anhydride) graft polymers have been found in the literature [6]. The aim of our study is to elucidate the influences of the reaction parameters on grafting MAH onto PcBR and to determine the thermodynamic parameters and the contact angle of the graft polymer obtained. Both the bulk and surface properties of the polymer are promising for application of PcBR-*g*-MAH.

EXPERIMENTAL

Material

Polybutadiene (high-*cis*-1,4 content, Mooney viscosity 46) from Beining Yanshan Petrochemical Company was used. Benzoyl peroxide (BPO) and 2,2-azo-bis-isobutyronitrile (AIBN) and other chemicals were used as received. Spectrally pure *n*-hexane, *n*-octane, *n*-nonane, and *n*-decane were used as probe molecules for gas chromatography.

Synthesis

The graft reaction was carried out in toluene at 65-70°C. Typical concentrations were 20 g/L, 3.06 mol/L, and 8.26 mmol/L for PcBR, MAH, and BPO (or AIBN), respectively. After the reaction was finished, the product was precipitated. The residual MAH was extracted with an acetone-toluene mixture, and the grafted PcBR was obtained after drying.

Characterization

A solution sample of the graft polymer in toluene was titrated with a KOH standard solution to determine the percent grafting.

The FT-IR spectra of solution-cast film specimens were measured on a Nicolet-5DX IR spectrometer.

Inverse Gas Chromatography Study

The column was prepared in the usual manner. The polymer was dissolved in tetrahydrofuran and then deposited on Glazed Carrier 302 (80-100 mesh) by slow evaporation of the solvent. After vacuum drying at 150°C, the coated support (8-10% loading) was packed into a stainless steel column (1000 mm long, 5 mm in o.d.). Retention data were obtained on a modified 102 Gas Chromtograph (Shanghai Analytical Instrument).

Determination of the Contact Angle Against Water

The contact angle was estimated on the sample plate of a ERM-422 goniometer at 18°C.

RESULTS AND DISCUSSION

Graft Copolymerization of MAH onto PcBR

There is no evidence for MAH homopolymerization in toluene at 70°C. Therefore, the grafted PcBR probably contains single pendent MAH units. The overall mechanism of graft polymerization of MAH onto PcBR can be shown as follows.

Decomposition of initiator:

$$I \rightarrow R^{\cdot} \tag{1}$$

Main-chain polymer radical formation:

$$R^{\cdot} + P_0H \rightarrow RH + P_0^{\cdot} \tag{2}$$

Formation of grafted polymer radical:

$$P_0^{\cdot} + M \rightarrow P_0M^{\cdot} \tag{3}$$

Termination by disproportionation:

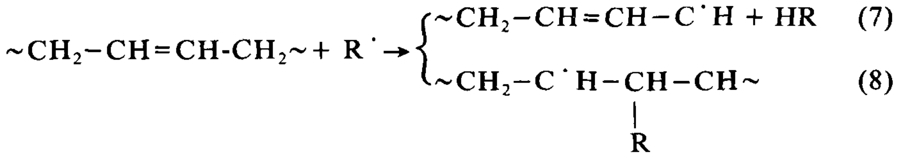
$$P_0^{\cdot} + P_0^{\cdot} \rightarrow \tag{4}$$

$$P_0^{\cdot} + P_0^{\cdot}M \rightarrow \tag{5}$$

$$P_0^{\cdot}M + P_0^{\cdot}M \rightarrow \tag{6}$$

and crosslinking through the same reactions (4 and 5) leading to coupling, where I is the initiator, $R^{\cdot}$ is the initiator fragment radical, M is MAH, P_0H is PcBR, $P_0^{\cdot}$ is the PcBR radical, and $P_0M^{\cdot}$ is the radical composed of $P_0^{\cdot}$ with multiple single units of MAH.

Reaction (2) is important for the formation of radicals on the main chain. In addition to abstraction of α-hydrogen from PcBR by the initiator fragment radical R$^{\cdot}$ (Eq. 7), the radical is able to add to the double bond of the PcBR chain (Eq. 8) [2], depending on the reactivity of R$^{\cdot}$, i.e., the type of initiator:



$$\sim CH_2-CH=CH-CH_2\sim + R^{\cdot} \rightarrow \begin{cases} \sim CH_2-CH=CH-C^{\cdot}H + HR & (7) \\ \sim CH_2-C^{\cdot}H-\underset{\displaystyle R}{\underset{|}{CH}}-CH\sim & (8) \end{cases}$$

Figure 1 depicts the effect on the type of initiator of the extent of grafting. These data indicate that the grafting reactivity of BPO is larger than that of AIBN, due to the resonance stabilization of the $C-\underset{C\ \ CN}{C^{\cdot}}$ radical being above that of the benzoyl radical. The IR spectra (Fig. 2) reveal that the

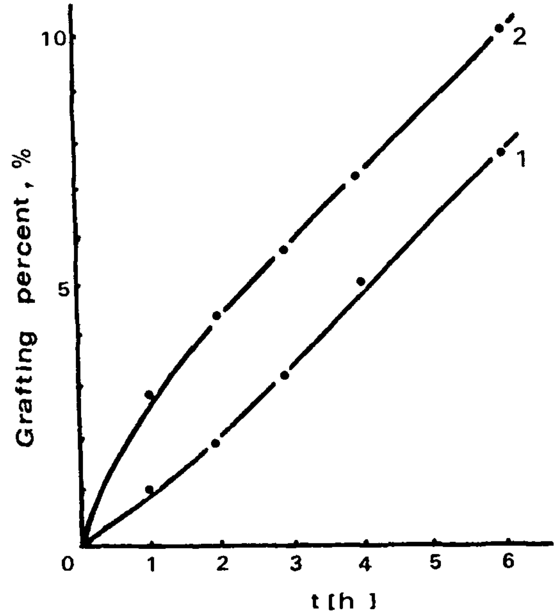


FIG. 1. Influence of type of initiator on grafting. [PcBR] = 20 g/L; [MAH] = 3.06 mol/L. Initiator: 1, [AIBN] = 8.26 mmol/L; 2, [BPO] = 8.26 mmol/L.

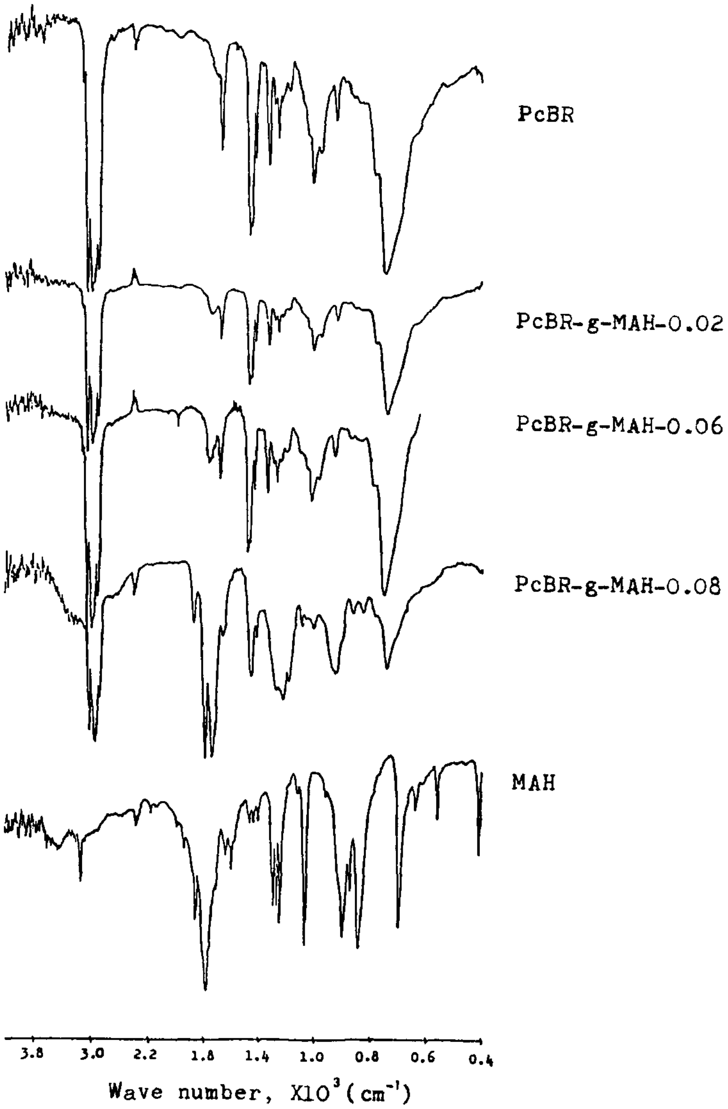


FIG. 2. FT-IR spectra of PcBR-g-MAH (BPO initiator).

doublet at 1780 and 1860 cm^{-1}, which is characteristic of the anhydride, shifts to somewhat lower wavenumbers, 1750 and 1770 cm^{-1}, for the grafted PcBR, and their intensities increase with grafting.

Moreover, changes in the ratio of the integrated intensities of the characteristic peak for the *cis*-vinylene structure at 740.7 cm^{-1}, $I_{(=CH)}$ [7], to that of the $-CH_2$ twisting vibration at 1450.6 cm^{-1}, $I_{(-CH_2)}$, i.e., $I_{(=CH)}/I_{(-CH_2)}$, is different for AIBN (2.35) and for BPO initiation (4.19) compared to the original ratio of PcBR (3.43), although the extent of grafting is different in the two cases (Table 1).

In the case of AIBN, the ratio $I_{(=CH)}/I_{(-CH_2)}$ decreases due to the addition of a radical to the double bond of the PcBR chain. This result is consistent with that of Yamaji [2]. As for BPO, the increase in the ratio is attributed to reduction either of just $I_{(-CH_2)}$ or of both $I_{(-CH_2)}$ and $I_{(=CH)}$. These correspond to the two initiation mechanisms, hydrogen abstraction (Eq. 7) and addition to the double bond (Eq. 8).

Influence of Reaction Parameters

Reaction Temperature

The extent of grafting increased with increasing temperature (Figs. 3 and 4), presumably because of the reduction of the half life of BPO with rising temperature, which would increase the number of $P_0^{\cdot}$ radicals (Eq. 3). When the temperature was over 70°C, partial crosslinking occurred according to Eq. (6).

TABLE 1. Ratio of Integrated IR Intensities, $I_{(=CH)}/I_{(-CH_2)}$, for Grafted PcBR

Grafting, %	—	6.2	8.0
Initiator	—	BPO	AIBN
Ratio $\dfrac{I_{=CH}(740.7\ cm^{-1})}{I_{-CH_2}(1450.6\ cm^{1})}$	3.43	4.19	2.35

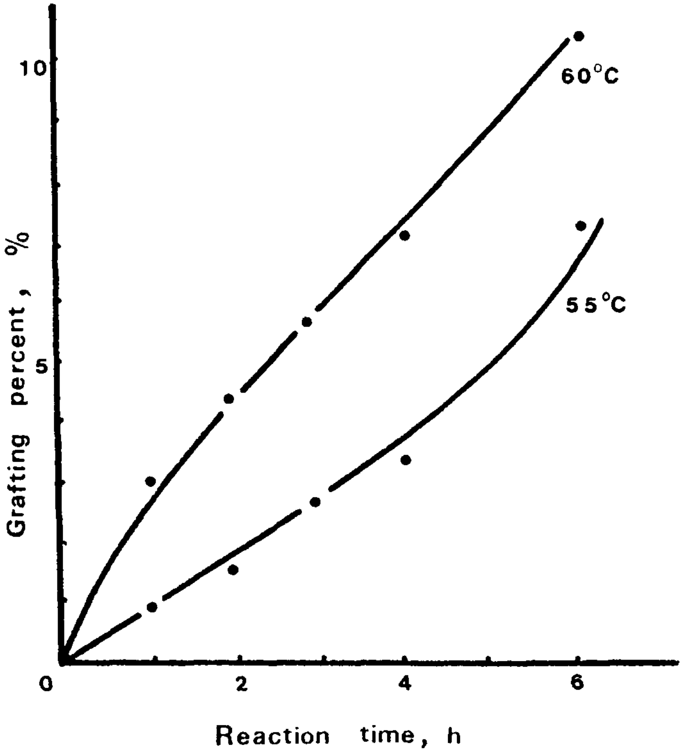


FIG. 3. Grafting versus reaction time. [PcBR] = 20 g/L; [MAH] = 3.06 mol/L; and [BPO] = 8.26 mmol/L.

Concentration of MAH

Figure 5 indicates that the extent of grafting increases with increasing concentration of MAH up to a certain value and then levels off.

Concentration of BPO

The influence of the concentration of BPO on grafting percent is very obvious (Fig. 6). At lower BPO concentration, an induction period (~1 h) is found (Curve 1), which implies that MAH has some retarding effect in our case. The induction period disappears as the BPO concentration is

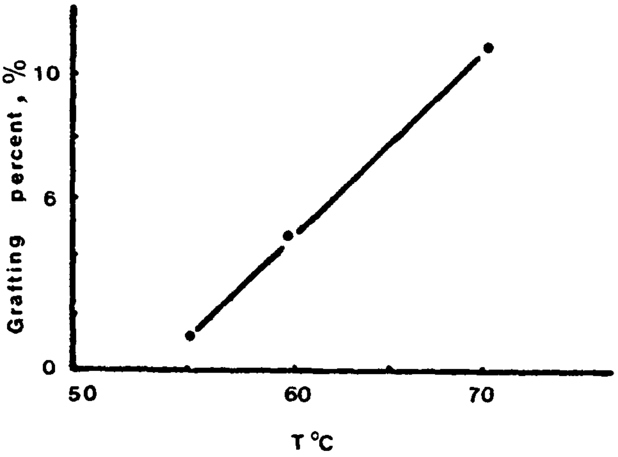


FIG. 4. Grafting as a function of reaction temperature. BPO initiator, 2 h.

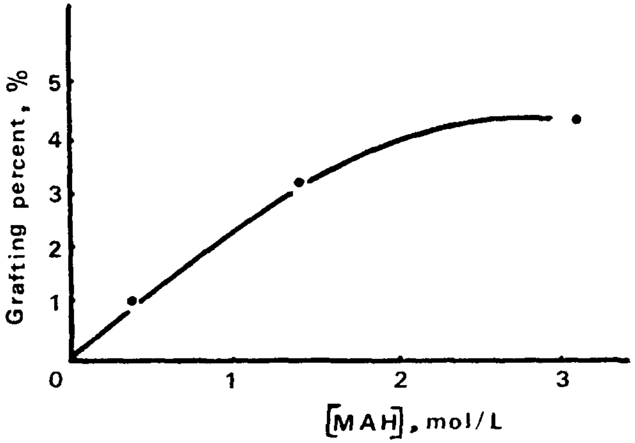


FIG. 5. Grafting as a function of MAH concentration. [PcBR] = 20 g/L; [BPO] = 8.26 mmol/L; 2 h, 60°C.

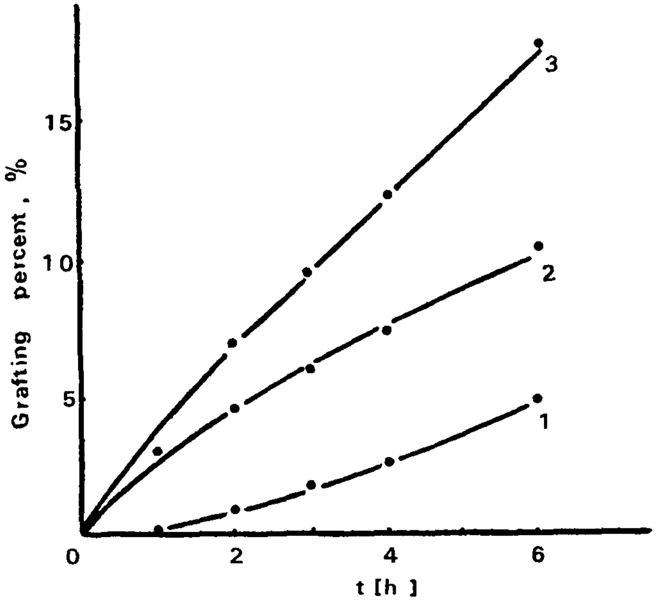


FIG. 6. Relation of grafting to BPO concentration. [PcBR] = 20 g/L; [MAH] = 3.06 mol/L; 60°C. BPO concentration: 1, 2.75 mmol/L; 2, 8.26 mmol/L; 3, 19.27 mmol/L.

raised, and the apparent grafting rate increases as well (Curve 2). When the concentration of BPO is raised further, the grafting rate rises further, and partially crosslinked product is obtained after 4 h reaction time (Curve 3). All these results are associated with rising concentration of $R^{\cdot}$, along with those of $P_0^{\cdot}$ and $P_0M^{\cdot}$, which can couple or lead to crosslinking.

Inhibition of Oxygen

Table 2 showed the inhibitive effect of oxygen on the reaction.

Interaction Parameter and Solubility Parameter

Inverse gas chromatography (IGC), also known as the molecular probe technique, uses a vapor phase component, **1** (the probe), to determine the

TABLE 2. The Effect of Oxygen on Grafting[a]

	Atmosphere		
	Oxygen	Air	Nitrogen
Grafting, %	0	2.17	4.56

[a][BPO] = 8.26 mmol/L; [PcBR] = 20 g/L; [MAH] = 3.06 mol/L; 60°C; 2 h.

TABLE 3. Interaction Parameter for the Grafted PcBR Probe

	Extent of grafting, %			
Probe	0	2.45	6.27	12.3
n-Hexane	0.52	0.54	0.61	0.68
n-Heptane	0.44	0.46	0.57	0.60
n-Octane	0.40	0.44	0.54	0.56
n-Nonane	0.38	0.42	0.53	0.56
n-Decane	0.37	0.42	0.51	0.54

interaction between it and a nonvolatile polymer, 2 (PcBR), in the stationary phase. The method leads to the χ_{12} parameter, which characterizes the interaction of the vapor phase with PcBR. χ_{12} can be calculated by the expression derived from the Flory-Huggins lattice approximation:

$$\chi_{12} = \ln\left(\frac{273.16RV_2}{P^\circ V_g V_1}\right) - 1 - \frac{P^\circ}{RT}(B_{11} - V_1) \tag{9}$$

where V_1 and V_2 are the molar volumes of the probe and the specific volume of PcBR, respectively; B_{11} is the second virial coefficient of the gaseous probe; and P° is its vapor pressure at temperature T. The results in Table 3 show that χ_{12} for PcBR-*g*-MAH and nonpolar *n*-alkane increases with increasing grafting percent.

On combining the Flory-Huggins theory with the solubility parameter concept developed by Hildebrand, one obtains

$$\chi_{12} = V_1(\delta_1 - \delta_2)^2/RT + \beta, \tag{10}$$

TABLE 4. Solubility Parameter at 130°C

Grafting, %	0	2.45	6.17	12.3
δ, (cal/mL)$^{1/2}$	6.49	6.58	6.68	7.00

where δ_1 and δ_2 are the solubility parameters for probe and PcBR, respectively; and β is the correction for the noncombinatorial entropy of mixing [10].

DiPaola-Baranyi and Guillet [11] rearranged Eq. (10) for $\beta = 0$ to give

$$(\delta_1{}^1/RT - \chi_{12}/V_1) = (2\delta_2/RT)\delta_1 - \delta_2{}^2RT. \tag{11}$$

Thus a plot of $(\delta_1{}^2/RT - \chi_{12}/V_1)$ versus δ_1 would give $2\delta_2/RT$ as the slope. Values of δ_2 for PcBR obtained by this method (Table 4) are not identical with that conventionally measured by swelling, solubility, or surface tension data (8.1) [12] since these are obtained at high concentrations of the probe while, in the present case, the probe is at infinite dilution in the polymer [12].

Contact Angle Against Water

The contact angle data in Table 5 show that the angle decreases with the extent of grafting, in line with the increase in polarity.

CONCLUSIONS

In comparison to AIBN, BPO is a better initiator for grafting maleic anhydride onto high *cis*-polybutadiene rubber. The extent of grafting is in the range of 2–12%, depending on the reaction parameters. The tempera-

TABLE 5. Contact Angle Against Water at 18°C

Grafting, %	0	2.45	6.27	8.00
Contact angle	88°	87°	85°	80°

ture should be below 70°C to avoid gel formation. The interaction parameter of the grafted PcBR and probe molecules and solubility parameter of PcBR-*g*-MAH increase with the extent of grafting, while the contact angle against water decreases.

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