

Polybutadiene Grafting and Crosslinking in High-Impact Polystyrene Bulk Thermal Process

FRED M. PENG, *Monsanto Chemical Company,
Springfield, Massachusetts 01151*

Synopsis

The grafting and the crosslinking of polybutadiene during the bulk thermal polymerization of high-impact polystyrene were studied. The kinetic equations for these two reactions were derived by the use of the moments of the distribution functions. This kinetic model indicates that both the density of grafting and the degree of crosslinking increase with the increasing temperature of polymerization and, most significantly, with the increasing conversion of styrene.

INTRODUCTION

In elastomer-modified polyblend systems, the morphology and the structure of the dispersed elastomer phase are two of the most important parameters influencing the product properties, i.e., impact and tensile strengths, surface appearance, and melt viscosity, etc. For high-impact (HI) polystyrene (PS) made by a bulk or a solution process, the elastomer phase morphology is determined during the initial stage of the polymerization before phase inversion¹ is completed. The factors determining the morphology have been comprehensively described.²⁻¹³ However, the structure, with respect to the grafts and the crosslinks, is difficult to quantify and study, especially when the conversion is high and the elastomer is crosslinked. Yet, these two structural parameters are crucial to the properties. Thus, this kinetic model study on the grafting and the crosslinking of the polybutadiene phase of HIPS was undertaken to appreciate these two reactions compelled by the thermal polymerization of styrene.

The grafting of styrene onto elastomers has been studied by numerous investigators.¹⁴⁻¹⁷ The influence of the elastomer phase structures on mechanical properties has been examined.^{12,13,18-22} Several kinetic models for the grafting reaction have been derived by various approaches.²³⁻²⁸ In this article, the kinetic model for the grafting and the crosslinking of polybutadiene of HIPS was developed by the use of the moments of the distribution functions. Emphasis was placed upon the final stage of the polymerization toward high conversions and high temperatures that have significant commercial process implications.

EXPERIMENTAL

Materials

The polybutadiene used was Diene 55NAF by Firestone Synthetic Rubber and Latex Co., with $M_w = 237,000$ and $M_n = 104,000$. Styrene monomer was

from Monsanto Co.; Polygard [tri(mixed mono- and di-nonylphenyl) phosphite], Uniroyal, Inc. All materials were used as received without further purification.

Polymerization

Five percent by weight of polybutadiene and 0.15% by weight of Polygard were dissolved in styrene monomer purged with nitrogen. This solution was first polymerized thermally in a continuous stirred tank reactor at 150°C at ca. 23% conversion of styrene. This partially polymerized and phase-inverted syrup was cooled to room temperature, transferred to 5-mm glass tubes, and sealed under nitrogen. Subsequently, further polymerization was carried out at 150°C in an oil bath to various degrees of conversion.

Determination of Polybutadiene Graft and Crosslink Levels

The polymer was dispersed overnight in a 50/50 by volume of MEK/DMF mixed solvent in a glass bottle on a shaker. Then the dispersion was transferred quantitatively to the stainless steel tube and ultracentrifuged to separate the gel from the soluble PS matrix. The gel was extracted once more with the mixed solvent and finally with methanol. The wet gel was dried at vacuum with nitrogen purge at 60°C for 6 h or overnight. The graft level was calculated by the weight of the isolated dried gel and reported as percent by weight of polybutadiene.

As evidenced by electron micrographs, the elastomer phase of HIPS contains a large volume of PS droplets that can be made of both grafted and ungrafted PS. It will be difficult for the included ungrafted PS to diffuse across the crosslinked elastomer boundaries during the solvent extraction. Thus, the graft levels measured likely embody not only the grafted but also the ungrafted but included PS.

The dried gel was then swollen overnight with toluene in the tube on a gentle vibrator. It was ultracentrifuged, and the supernatant liquid removed; the weight of the wet swollen gel was recorded. Finally, the swollen gel was redispersed in methanol, ultracentrifuged, and dried. The swelling index (inversely proportional to the crosslinking density of the gel) was calculated as the weight ratio of the wet swollen to the dried gel. Tests demonstrated that the drying of the gel for the graft analysis, prior to the swelling measurement, did not alter its swelling index. This was consistent with the Table I results: in the absence of styrene monomer, heating alone at high temperature did not cause the polybutadiene to crosslink.

RESULTS AND DISCUSSION

The kinetic model presented here is based on that for styrene thermal polymerization with the incorporation of grafting and crosslinking reactions. The grafting of polybutadiene is initiated by the abstraction of allylic hydrogens by radicals (but not via the double bonds),²⁹⁻³¹ followed by the growth of the PS graft chains. The crosslinking is accomplished by the combination of two graft-chain radicals. In the absence of styrene monomer, heating alone did not induce

TABLE I
Effect of Residual Styrene on Swelling Index of the Polybutadiene Phase upon Heating

Residual styrene (wt %)	Swelling index	
	Initial	After heat treated ^a
0 ^b	∞^c	∞^c
0.15 ^d	19	14
10	∞^c	11

^a One hour at 210°C under nitrogen in glass tube.

^b Attained by devolatilizing a 60% conversion syrup at low temperatures under nitrogen purge.

^c Practically soluble in toluene.

^d Attained as in note b but using a high conversion syrup.

the polybutadiene to crosslink, as mentioned previously and shown in Table I. Thus, the double bonds of polybutadiene do not participate directly in grafting or crosslinking in the thermal polymerization of HIPS. Therefore, the mechanistic schemes of the grafting and the crosslinking reactions described are plausible.

The styrene thermal polymerization kinetics are given in Appendix I. The details of the grafting and the crosslinking kinetics are developed in Appendix II. The numerical solution was carried out for four temperatures to 98% conversion. The rate constant for transfer to polybutadiene (abstraction of allylic hydrogen) was taken as 1/13.5 of that for the styrene polymerization to fit the experimental data at 150°C, as shown in Figure 4. It is conceivable that these two transfer reactions could have different activation energies, however. In addition, as mentioned previously, the measured graft levels likely contained the included but ungrafted PS. Hence, the results shown might convey not the quantitative but rather the qualitative nature of these two reactions.

Figures 1 and 2 show the relative sites grafted and crosslinked, respectively. Both of these two reacted sites increased with temperature and drastically with conversion. As conversion increases, grafting and consequently crosslinking are favored over styrene homopolymerization, simply because grafting sites progressively become more available relative to styrene monomer. At 150°C, the swelling index was unmeasurably high until the conversion exceeded 90%, and finally attained a value of 12 when conversion reached 98+%. This agreed well with the results shown in Figure 2 that crosslinking did not proceed substantially until conversion was above 90% at 150°C. It was reported that crosslinking was not detectable by this toluene swelling technique until styrene conversion exceeded 80%, when the polymerization was carried out at 85–95°C with initiators.³²

Figure 3 is the combination of those two graphs, showing the relationship between grafting and crosslinking. Figure 4 illustrates the graft level (as weight percent of polybutadiene) as influenced by conversion and temperature. As shown, the slight decrease in graft level with increasing temperature was attributed to the decrease of the PS graft-chain molecular weight with increasing temperature in spite of the substantial increase in graft density (Fig. 1). Figure 5 indicates the graft level vs. the crosslinked sites at various temperatures and conversions.

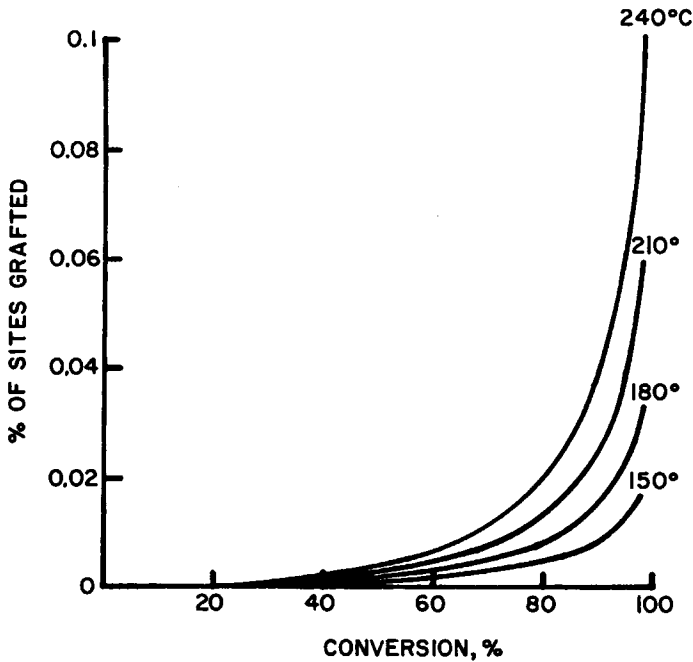


Fig. 1. Grafted sites vs. conversion.

It has been reported that the rubber efficiency for improving toughness is enhanced by increased grafting and reduced crosslinking.^{12,13,18,20,22} Thus, based on the results of this kinetic model study, it can be concluded that in order to maximize grafting and minimize crosslinking, it is desirable to carry out the polymerization to high conversion and at low temperature.

CONCLUSIONS

The kinetic model predicts the generally expected nature of the grafting and the crosslinking reactions of HIPS with respect to temperature and conversion, i.e., both reactions advance with the increase of these two polymerization conditions.

In order to attain high level of grafting but low degree of crosslinking, the thermal polymerization of HIPS may be carried out to high conversion but at low temperature.

This writer appreciates the experiment carried out by L. Gerasimow and the encouragement and support given by R. W. Jones.

APPENDIX I

Styrene Bulk Thermal Polymerization Kinetics

Initiation

The thermal initiation of styrene polymerization is described.³³ Both the second- and the third-order initiation mechanisms are consistent with the data

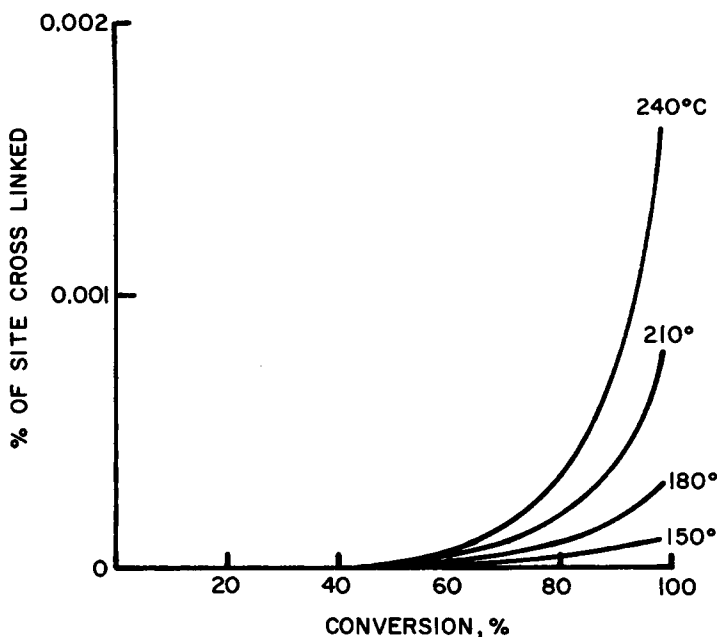
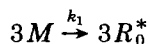
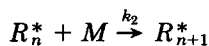
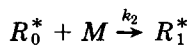


Fig. 2. Crosslinked sites vs. conversion.

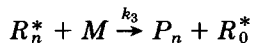
of the observed distribution moments.³⁴ A form of the third-order initiation was suggested³⁶: $3M \rightarrow 2R_0^*$. It was proposed the Diels-Alder adduct to be the intermediate for the styryl radical formation by thermal initiation.³⁶ For this kinetic model, the following form of the third-order initiation was used:



Propagation

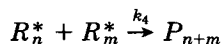


Transfer



(Transfer to oligomers was not considered explicitly here but accounted for by making this transfer constant as a function of both temperature and conversion.)

Termination



M = styrene monomer conc., mol/L

M_0 = initial styrene monomer conc. = 8.05

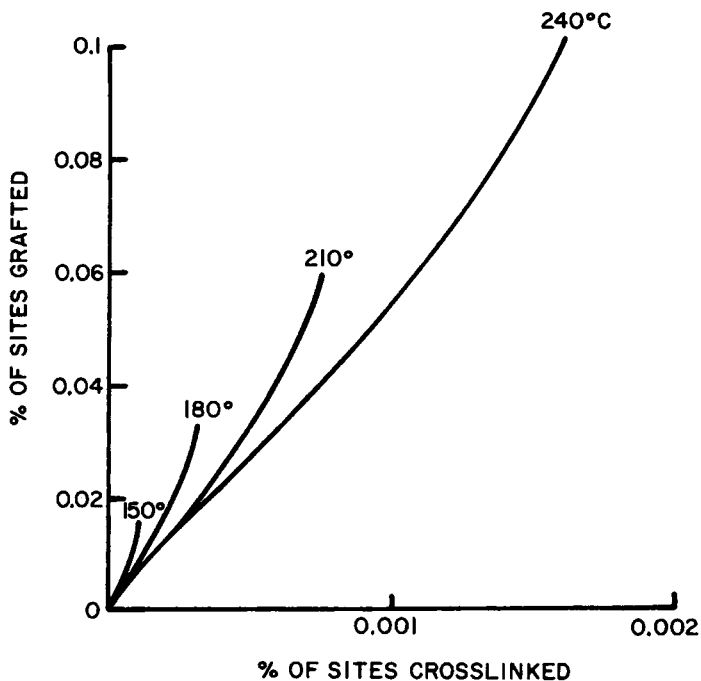


Fig. 3. Grafting vs. crosslinking.

R_0^* = styryl radical conc.

R_n^* = polystyryl radical conc. of n degree of propagation

P_n = polystyrene conc. of n degree of polymerization

X = conversion, fraction

T = temperature, K

$k_1 = 2.3 \times 10^6 \exp(-15005/T)$, $(\text{mol/L})^{-2} \text{s}^{-1}$

$k_2 = 6.609 \times 10^5 \exp(-2600/T)$, $(\text{mol/L})^{-1} \text{s}^{-1}$

$k_3 = 2.568 \times 10^5 \exp[-3504/T - 4000X(1/T - 1/373) - 1996/373]$, $(\text{mol/L})^{-1} \text{s}^{-1}$

$k_{40} = 1.255 \times 10^9 \exp(-844/T)$, $(\text{mol/L})^{-1} \text{s}^{-1}$

$A_1 = 1000X$

$A_2 = 4.42549 \exp(-1.9837X)$

For temperature $\leq 130^\circ\text{C}$ and all X ,

$$k_4 = k_{40} \exp[-X A_2 \exp(A_1/T)]$$

For temperature $> 130^\circ\text{C}$ and $X < 0.65$,

$$k_4 = k_{40} \exp[-X A_2 \exp(A_1/403)]$$

For temperature $> 130^\circ\text{C}$ and $X \geq 0.65$,

$$k_4 = k_{40} \exp[-X A_2 \exp(A_1/T)]$$

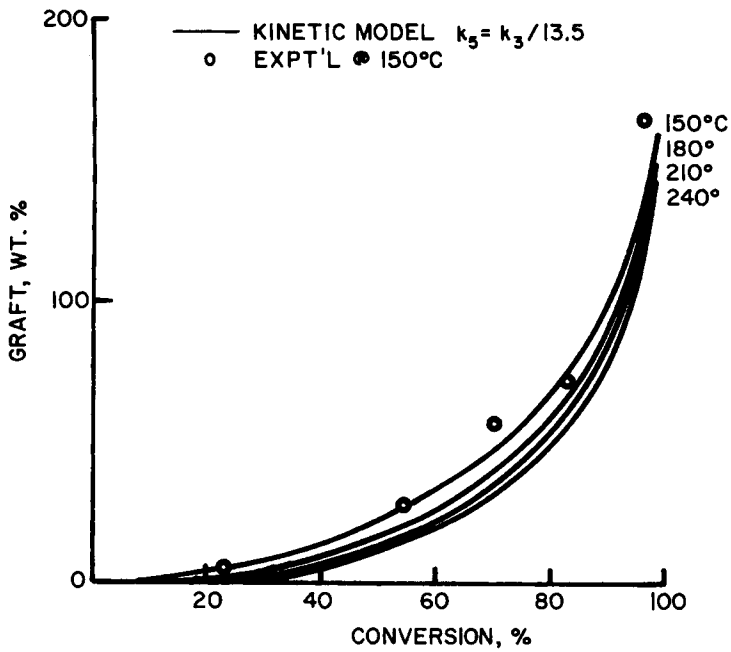


Fig. 4. Graft level vs. conversion.

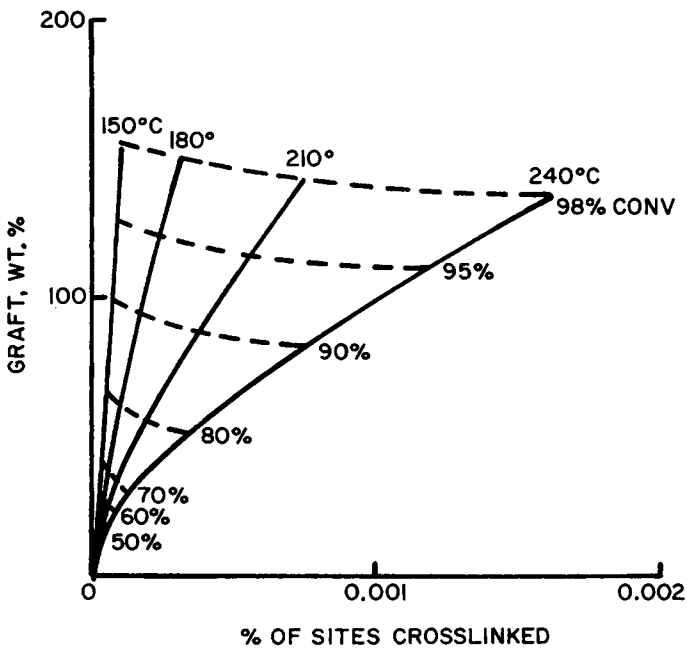


Fig. 5. Graft level vs. crosslinking.

These rate constant expressions were derived from the experimental thermal polymerization data.³⁷ The dependency of k_4 on X accounted for the gel (Trommsdorff) effect; that of k_3 on X was for fitting of the molecular weight data and accounted for the effect of transfer to oligomers. Other sources of styrene polymerization kinetics are also available.³⁸

APPENDIX II

Derivation of the Kinetic Model for Polybutadiene Grafting and Crosslinking Reactions in the Presence of Styrene Bulk Thermal Polymerization

Both the grafting and the crosslinking reactions for polybutadiene were incorporated into the kinetic model for styrene homopolymerization described in Appendix I. The following propositions were made:

1. The effects due to the presence of polybutadiene were neglected, e.g., density and viscosity, and hence the change in volume and the enhancement of Trommsdorff (gel) effect.

2. The very small partitioning of styrene monomer toward polybutadiene³⁹ was neglected. Thus, it was treated as a homogeneous system.

3. The first step of the thermal grafting reaction was the formation of polybutadiene radical through the abstraction of allylic hydrogen by styryl or polystyryl radical,²⁹⁻³¹ i.e., the transfer of radical to polybutadiene. Growth of the graft chain was similar to the propagation of the polystyryl radical. Combination of a graft-polystyryl radical and a homopolystyryl radical formed a terminated graft chain; combination of two graft-polystyryl radicals formed a crosslink chain.

The polybutadiene used had ca. 10% of vinyl content. These vinyl groups are reactive and expected to copolymerize with styrene, providing a second route to grafting and crosslinking. However, both routes to these two reactions would lead to the same results. Thus, the vinyl groups were not treated separately to simplify the analysis.

4. The reactivities of the graft-polystyryl and the homopolystyryl radicals were the same, having the same corresponding propagation, transfer, and termination rate constants.

5. The chain transfer constant to rubber was assigned as equal to 1/13.5 times of that to styrene monomer to fit the data at 150°C, as shown in Figure 4. (It is conceivable that these two types of chain transfer reaction could possibly have different activation energies, however.)

6. Stationary state free radical reactions.

7. Constant concentration of graftable sites. (At the graft level of 150%, the sites both grafted and crosslinked were merely less than 0.1% of the initial available sites.)

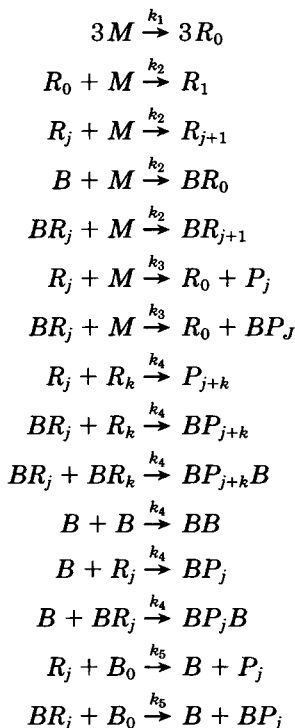
The kinetic schemes and rate expressions follow the definition of the concentrations of various species:

M_0 = initial styrene monomer

M = styrene monomer

R_0 = styryl radical

- R_j = homopolystyryl radical of j degree of propagation
- B_0 = polybutadiene graftable sites (allylic hydrogens)
- B = allylic hydrogen abstracted polybutadiene radical
- BR_j = graft-polystyryl radical of j degree of propagation
- P_j = polystyrene of j degree of polymerization
- BP_j = polystyrene graft chain of j degree of polymerization
- BP_jB = polystyrene crosslink chain of j degree of polymerization



$$\frac{dM}{dt} = -3k_1M^3 - k_2M \left[\sum_{j=0}^{\infty} (R_j + BR_j) + B \right] - k_3M \sum_{j=0}^{\infty} (R_j + BR_j) \quad (1)$$

$$\begin{aligned}
 \frac{dR_j}{dt} = & [3k_1M^3 + k_3M \sum_{k=0}^{\infty} (R_k + BR_k)] \delta(j) - k_2M(R_j - R_{j-1}) \\
 & - k_3MR_j - k_4R_j \left[\sum_{k=0}^{\infty} (R_k + BR_k) + B \right]^* - k_5B_0R_j \quad (2)
 \end{aligned}$$

where $\delta(j) = 1$ for $j = 0$ and $\delta(j) = 0$ for $j \neq 0$. (Strictly, the term marked with an asterisk should be $-k_4R_j \left[\sum_{k=0}^{\infty} (R_k + BR_k) + B + R_j \right]$, as the disappearance of R_i is concerned, $dR_i/dt = -2k_4R_i^2$. However, R_j is neglected in general as $R_j \ll \sum_{k=0}^{\infty} R_k$.)

$$\frac{dBR_j}{dt} = k_2MB\delta(j) - k_2M(BR_j - BR_{j-1}) - k_3MBR_j - k_4BR_j \left[\sum_{k=0}^{\infty} (R_k + BR_k) + B \right] - k_5B_0BR_j \quad (3)$$

$$\frac{dB}{dt} = -k_2MB - k_4B \left[\sum_{k=0}^{\infty} (R_k + BR_k) + 2B \right] + k_5B_0 \sum_{k=0}^{\infty} (R_k + BR_k) \quad (4)$$

$$\frac{dP_j}{dt} = k_3MR_j + \left(\frac{k_4}{2} \right) \sum_{n=0}^j R_{j-n}R_n + k_5B_0R_j \quad (5)$$

$$\frac{dBP_j}{dt} = k_3MBR_j + k_4 \sum_{n=0}^{\infty} BR_{j-n}R_n + k_4(B)R_j + k_5B_0BR_j \quad (6)$$

$$\frac{dBB}{dt} = k_4B^2 \quad (7)$$

$$\frac{dBP_jB}{dt} = \left(\frac{k_4}{2} \right) \sum_{n=0}^{\infty} BR_{j-n}BR_n + k_4(B)BR_j \quad (8)$$

Equations (1)–(8) can be transformed by using the Z transformation defined as

$$P(Z) = \sum_{n=0}^{\infty} Z^{-n}P_n$$

$$R(Z) = \sum_{n=0}^{\infty} Z^{-n}R_n$$

$$BR(Z) = \sum_{n=0}^{\infty} Z^{-n}BR_n$$

$$BP(Z)B = \sum_{n=0}^{\infty} Z^{-n}BP_nB, \text{ etc.}$$

$$dM/dt = -3K_1M^3 - (k_2 + k_3)M[R(1) + BR(1)] - k_2MB \quad (9)$$

$$dR(Z)/dt = 3k_1M^3 + k_3M[R(1) + BR(1) - R(Z)] - k_2M(1 - Z^{-1})R(Z) - k_4[R(1) + BR(1) + B]R(Z) - k_5B_0R(Z) \quad (10)$$

$$dBR(Z)/dt = -k_2M(1 - Z^{-1})BR(Z) - k_3MBR(Z) + k_2MB - k_4[R(1) + BR(1) + B]BR(Z) - k_5B_0BR(Z) \quad (11)$$

$$dB/dt = k_5B_0[R(1) + BR(1)] - k_2MB - k_4B[R(1) + BR(1) + 2B] \quad (12)$$

$$dP(Z)/dt = k_3MR(Z) + (k_4/2)[R(Z)]^2 + k_5B_0R(Z) \quad (13)$$

$$dBP(Z)/dt = k_3MBR(Z) + k_4[BR(Z) + B]R(Z) + k_5B_0BR(Z) \quad (14)$$

$$dBB/dt = k_4B^2 \quad (15)$$

$$dBP(Z)B/dt = (k_4/2)[BR(Z)]^2 + k_4(B)BR(Z) \quad (16)$$

According to the Z transforms, the moments are defined as

$$\begin{aligned}
 U_k &= \sum_{n=0}^{\infty} n^k P_n = \lim_{Z \rightarrow 1} \frac{d^k P(Z)}{d(\ln Z^{-1})^k} \\
 BU_k &= \sum_{n=0}^{\infty} n^k BP_n = \lim_{Z \rightarrow 1} \frac{d^k BP(Z)}{d(\ln Z^{-1})^k} \\
 BU_k B &= \sum_{n=0}^{\infty} n^k BP_n B = \lim_{Z \rightarrow 1} \frac{d^k BP(Z)B}{d(\ln Z^{-1})^k} \\
 T_k &= \sum_{n=0}^{\infty} n^k R_n = \lim_{Z \rightarrow 1} \frac{d^k R(Z)}{d(\ln Z^{-1})^k} \\
 BT_k &= \sum_{n=0}^{\infty} n^k BR_n = \lim_{Z \rightarrow 1} \frac{d^k BR(Z)}{d(\ln Z^{-1})^k}
 \end{aligned}$$

Consequently, $U_1 + BU_1 + BU_1 B$ is the total amount of monomer polymerized; U_1/U_0 and U_2/U_1 are the number and the weight average degrees of polymerization of the matrix polystyrene, respectively; and $(BU_1 + BU_1 B)/(BU_0 + BU_0 B)$ and $(BU_2 + BU_2 B)/(BU_1 + BU_1 B)$ are the number and the weight average degrees of polymerization of the graft chain, respectively. The equations of moments corresponding to Eqs. (9)–(16) are listed below: (Since $B \ll \sum_{j=0}^{\infty} BR_j = BT_0$, B can be neglected as compared with BT_0 , and is so indicated with an underline wherever applicable.)

$$dM/dt = -3k_1 M^3 - k_2 M(T_0 + BT_0 + \underline{B}) - k_3 M(T_0 + BT_0) \tag{17}$$

$$dT_0/dt = 3k_1 M^3 + k_3 MBT_0 - [k_4(T_0 + BT_0 + \underline{B}) + k_5 B_0] T_0 \tag{18}$$

$$dT_1/dt = k_2 MT_0 - [k_3 M + k_4(T_0 + BT_0 + \underline{B}) + k_5 B_0] T_1 \tag{19}$$

$$dT_2/dt = k_2 M(2T_1 + T_0) - [k_3 M + k_4(T_0 + BT_0 + \underline{B}) + k_5 B_0] T_2 \tag{20}$$

$$dB/dt = -[k_2 M + k_4(T_0 + BT_0 + 2\underline{B})] B + k_5 B_0(T_0 + BT_0) \tag{21}$$

$$dBT_0/dt = k_2 MB - [k_3 M + k_4(T_0 + BT_0 + \underline{B}) + k_5 B_0] BT_0 \tag{22}$$

$$dBT_1/dt = k_2 MBT_0 - [k_3 M + k_4(T_0 + BT_0 + \underline{B}) + k_5 B_0] BT_1 \tag{23}$$

$$\begin{aligned}
 dBT_2/dt &= k_2 M(2BT_1 + BT_0) \\
 &\quad - [k_3 M + k_4(T_0 + BT_0 + \underline{B}) + k_5 B_0] BT_2 \tag{24}
 \end{aligned}$$

$$dU_0/dt = [k_3 M + (k_4/2) T_0 + k_5 B_0] T_0 \tag{25}$$

$$dU_1/dt = (k_3 M + k_4 T_0 + k_5 B_0) T_1 \tag{26}$$

$$dU_2/dt = (k_3 M + k_4 T_0 + k_5 B_0) T_2 + k_4 T_1^2 \tag{27}$$

$$dBU_0/dt = k_4(BT_0 + \underline{B})T_0 + (k_3M + k_5B_0)BT_0 \quad (28)$$

$$dBU_1/dt = k_4(BT_0 + \underline{B})T_1 + (k_3M + k_4T_0 + k_5B_0)BT_1 \quad (29)$$

$$dBU_2/dt = k_4(BT_0 + \underline{B})T_2 + 2k_4(T_1)BT_1 + (k_3M + k_4T_0 + k_5B_0)BT_2 \quad (30)$$

$$dBB/dt = k_4B^2 \quad (31)$$

$$dBU_0B/dt = k_4(BT_0/2 + \underline{B})BT_0 \quad (32)$$

$$dBU_1B/dt = k_4(BT_0 + \underline{B})BT_1 \quad (33)$$

$$dBU_2B/dt = k_4(BT_1)^2 + k_4(BT_0 + \underline{B})BT_2 \quad (34)$$

From the definition of moments, the conversion of the monomer is

$$\begin{aligned} X &= (U_1 + BU_1 + BU_1B + T_0 + BT_0)/M_0 \\ &\simeq (U_1 + BU_1 + BU_1B)/M_0 \end{aligned} \quad (35)$$

as $(T_0 + BT_0) \ll (U_1 + BU_1 + BU_1B)$, where X = fraction of conversion and M_0 = initial monomer concentration = 8.05.

$$dX/dt = (1/M_0)d(U_1 + BU_1 + BU_1B)/dt \quad (36)$$

Substituting eqs. (26), (29), and (33) in (36),

$$dX/dt = (1/M_0)[k_3M + k_4(T_0 + BT_0) + k_5B_0](T_1 + BT_1) \quad (37)$$

Assuming stationary state, i.e., eqs. (18)–(24) are equal to zero, and combining eqs. (19), (23), and (37),

$$\begin{aligned} dX/dt &= k_2(M/M_0)(T_0 + BT_0) \\ &= k_2(1 - X)(T_0 + BT_0) \end{aligned} \quad (38)$$

The rate of sites being crosslinked is

$$\begin{aligned} dS_x/dt &= 2d(BB + BU_0B)/dt \\ &= k_4(BT_0)^2 \end{aligned} \quad (39)$$

(The factor of 2 is due to the fact that one crosslinked chain takes two sites on the polybutadiene.)

The rate of sites being grafted and crosslinked is

$$\begin{aligned} dS_{gx}/dt &= d(BU_0 + S_x)/dt \\ &= [k_3M + k_4(T_0 + BT_0) + k_5B_0]BT_0 \end{aligned} \quad (40)$$

The graft level as weight percent of polybutadiene is

$$\begin{aligned}
 G &= (BU_1 + BU_1B)(104.14)(100)/(\text{wt. conc. of polybutadiene}) \\
 &= (BU_1 + BU_1B)(104.14)(100)/[(5\%/0.95)(8.05)(104.14)] \\
 &= (BU_1 + BU_1B)/0.004237 \qquad (41)
 \end{aligned}$$

Equations (18), (21), and (22) were solved simultaneously for T_0 and BT_0 first. Then T_1 , BT_1 , T_2 , and BT_2 were solved individually. Finally, the other solutions were obtained by numerical integration. The rate constants k_1 through k_4 as listed in Appendix I were used, and k_5 was set to be $k_3/13.5$ to fit the experimental data at 150°C shown in Figure 4.

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