

QUANTITATIVE ANALYSIS OF GRAFTING AND CROSSLINKING ON THERMAL BULK POLYMERIZATION OF HIGH IMPACT POLYSTYRENE

Joon-Yong Park and O Ok Park[†]

Department of Chemical Engineering, Korea Advanced Institute of Science & Technology,
373-1 Kusong-dong, Yusong-ku, Taejon 305-701, Korea

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Abstract—Analytic expressions for grafting of polystyrene (PS) onto polybutadiene (PBD) and crosslinking of PBD during thermal bulk polymerization of high impact polystyrene (HIPS) were derived by using moment distribution function based on Peng's kinetic scheme [1]. The ratio of chain transfer constant for PBD to that for styrene monomer, k_5/k_3 , was determined by the linear correlation between grafting efficiency (GE) and $\ln 1/(1-X)$ where X was the conversion of styrene. Both the GE and $\ln 1/(1-X)$ were determined from experiments. According to this correlation, the GE did not depend on the reaction temperature, which seemed that the temperature dependence was offset in the ratio of chain transfer constant for PBD to that for styrene monomer in this analytic expression. The degree of crosslinking drastically increased at high temperature ($\geq 190^\circ\text{C}$) and at high conversion such as 95%. With minor modification, these analytic formulas could be used for the polymerization using initiators. Furthermore, it will be useful to design the polymerization process.

INTRODUCTION

High impact polystyrene (HIPS) process has been well known industrially from 1950's and its essence is to improve its mechanical properties by reactive blending of rubbers with polystyrene (PS), especially polybutadiene (PBD) is the preferred rubber for several reasons. In other words, styrene monomer is polymerized under agitation with a small amount of PBD. PBD is initially dissolved in styrene, but after some conversion PBD phase is separated into its own phase along with increasing PS phase. The grafted PBD concentrates at the phase boundary, where it acts as a surfactant between two immiscible phases. When the volume of the dispersed PS phase is comparable with that of the continuous PBD phase, the phase inversion takes place and it shows the sigmoid curve of total viscosity [2-4]. During the phase inversion, morphology and size of PBD particle are determined and they are directly related to the final properties of HIPS such as mechanical properties and surface gloss [5-7]. Two major concerns during polymerization are; grafting of PS onto PBD, which causes better adhesion of PBD particle to PS matrix, and crosslinking be-

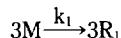
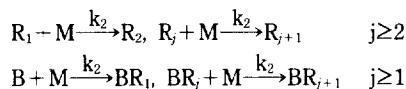
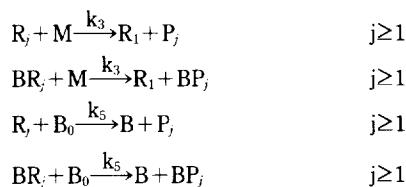
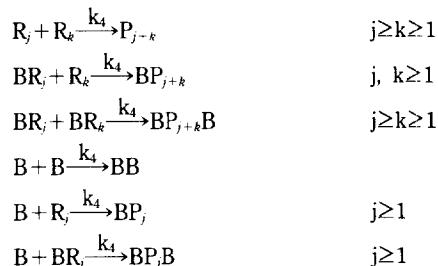
tween PBD and PBD with PS chains, which is not preferred for the mechanical properties [8, 9].

There have been a lot of studies for HIPS process [10], but quantitative model was not available until Peng reported his excellent paper on mathematical model for HIPS by utilizing PS polymerization data [1], although Brydon et al. [11, 12] studied the grafting of PS onto PBD in benzene solution based on the simple kinetic scheme. But Peng's scheme needed some complicated computations to predict grafting and crosslinking. Here a simplified analytical expression will be derived for the prediction of the amount of PS grafting onto PBD and the degree of crosslinking of PBD, which will be compared with some experimental data in order to confirm its validity.

THEORY

The kinetic model presented here was based on that for styrene thermal polymerization with the incorporation of grafting and crosslinking reaction [1]. For this kinetic model, the third-order initiation form was used and it was assumed that the grafted polystyryl radicals have the same reactivity as the homo polystyryl radicals.

[†]To whom all correspondences should be addressed.

Initiation**Propagation****Transfer****Termination**

M : Styrene monomer [mol/L]

R₁, R₂, ... : Styrene radicals

BR₁, BR₂, ... : Grafted styrene radicals

B₀ : PBD graftable sites (Allylic hydrogen)

B : Allylic hydrogen abstracted PBD radical

P₁, P₂, ... : Homo PS

BP₁, BP₂, ... : Grafted PS

BB, BP₁B, BP₂B, ... : Crosslinked PS

The grafting of PS onto PBD was initiated by the abstraction of allylic hydrogens of PBD by radical transfer, followed by the growth of the PS graft chains. The crosslinking was accomplished by the combination of two radicals at the end of grafted chain. It was known that the double bonds of PBD don't participate directly in grafting and crosslinking in the thermal polymerization HIPS [12, 13]. More detailed propositions were described in the reference 1.

The rate constant expressions were derived from the experimental thermal polymerization data [1]. Here k₃ and k₅ represent the chain transfer constant to styrene monomer and that to PBD. T is the temperature and X is the conversion of styrene.

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

$$\begin{aligned} k_2 &= 6.609 \times 10^5 \exp(-2600/T), \quad [\text{mol/L}]^{-1} \text{ s}^{-1} \\ k_3 &= 2.568 \times 10^5 \exp[-3504/T - 4000X(1/T - 1/373) \\ &\quad - 1996/373], \quad [\text{mol/L}]^{-1} \text{ s}^{-1} \\ &\quad \left[\begin{array}{l} k_{40} \exp[-X A_2 \exp(A_1/T)] \\ \text{Temperature} \leq 130^\circ\text{C} \text{ and all } X \end{array} \right] \\ k_4 &= \left[\begin{array}{l} k_{40} \exp[-X A_2 \exp(A_1/403)] \\ \text{Temperature} > 130^\circ\text{C} \text{ and } X < 0.65 \\ k_{40} \exp[-X A_2 \exp(A_1/T)] \end{array} \right] \\ &\quad \text{Temperature} > 130^\circ\text{C} \text{ and } X \geq 0.65 \\ \text{where, } k_{40} &= 1.255 \times 10^9 \exp(-884/T), \quad [\text{mol/L}]^{-1} \text{ s}^{-1} \\ A_1 &= 1000X \quad A_2 = 4.42549 \exp(-1.9837X) \end{aligned}$$

EXPERIMENTAL

Styrene monomer was purified by distillation under vacuum before every use. PBD used was 55A, made by Asahi Chem. Co., having M_w=483,000 and M_n=186,000.

First, PBD was dissolved in styrene monomer to the conc. of 6 wt%. The desired amount of the solution was charged into a long glass tube reactor and it was sealed tightly under nitrogen. The solution was polymerized thermally in a silicon oil bath at 130°C, 150°C, 170°C, and 190°C to various degree of conversion.

The polymer or the prepolymer syrup was dissolved in a 50/50 by volume of MEK (Methyl Ethyl Ketone)/DMF (Dimethylformamide) mixed cosolvent in a Poly-alomer (Nalge Co.) bottle on a shaker for 12h. And it was ultracentrifuged to separate the gel (PBD+PBD-g-PS) from the soluble PS matrix. The gel was washed once more with cosolvent and centrifuged. Finally it was extracted with methanol. The wet gel was dried under vacuum at 60°C for 8h. This gel probably included some of the free PS within the PBD particles as well as the chemical grafted PS. The graft efficiency (GE) was obtained by:

$$\begin{aligned} GE(\%) &= \frac{\text{wt of dried gel} - \text{wt of PBD}}{\text{wt of PBD}} \times 100 \\ &= \frac{\text{wt of grafted polystyrene}}{\text{wt of PBD}} \times 100 \quad (1) \end{aligned}$$

RESULTS AND DISCUSSION

The analytic formulas of grafting efficiency and cross-linked sites percent were derived from the thermal polymerization kinetics as shown in Appendix using the moment distribution function. Some approximations, with the comparison of the order of magnitude of each term including a rate constant, used to obtain the final results.

The GE was analytically derived as bellow

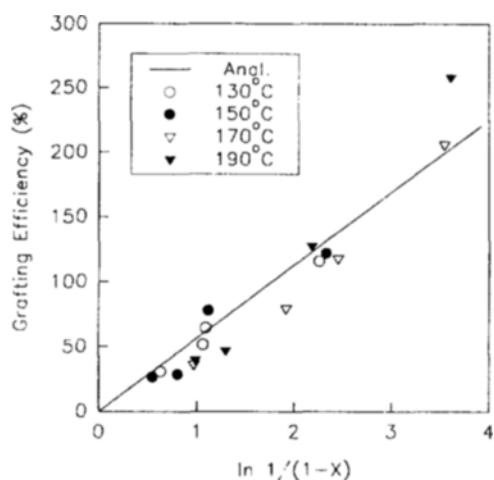


Fig. 1. Grafting efficiency (GE) as a function of $\ln 1/(1-X)$.

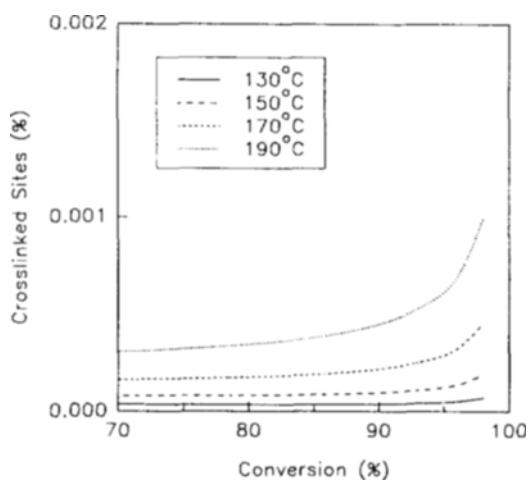


Fig. 2. Crosslinked sites as a function of conversion.

Table 1. The digitized data from Brydon et al. [12]'s result

$1/M_0$	M_0	$1/(GF-1)^{1/2}$	GF	$GF \cdot M_0$
0.2	5	1.06	0.11	0.55
0.35	2.86	1.11	0.19	0.5434
0.47	2.13	1.16	0.26	0.5538
0.67	1.49	1.23	0.34	0.5066

$$\frac{GE(\%)}{100} = f \frac{M_{St}}{M_{PBD}} \frac{k_5}{k_3} \ln \frac{1}{1-X} \quad (2)$$

where f was the graftability factor of allylic hydrogen of PBD by abstracting and it was influenced by the viscosity, M_{St} is the molecular weight of styrene monomer and M_{PBD} is the molecular weight of PBD unit. The value of GE from the experiment had a linear dependence on the $\ln 1/(1-X)$ and it was consistent with the analytical result of this work using $f k_5/k_3 = 0.292$ (Fig. 1). Furthermore, it is shown that there was no apparent dependence of GE on the reaction temperature. Both the styryl radical and the allylic radical from the abstraction reaction have resonance energies in the region of 84 kJ/mole and Brydon et al. had obtained the same trend [12]. Hence it was reasonable to expect that the rate constant ratio, k_5/k_3 , does not depend on the reaction temperature, because two activation energies could have comparable magnitudes.

The graftability factor of PBD should be less than 1 in bulk polymerization due to a viscosity effect, and it was possible to obtain the value of transfer constant

ratio from Brydon et al. [12]'s solution polymerization for $f=1$. Because the graftability factor, f , was considered on the basis of the interference of increased viscosity with the probability of styryl radicals transfer to allylic hydrogen of PBD in a thermal bulk process, it was reasonable that the graftability factor was unity in a solution process. By using the moment distribution function, graft fraction of PS (GF) could be represented as,

$$GF = \frac{\text{Grafted Polystyrene}}{\text{Total Polystyrene}} = \frac{k_5}{k_3} \frac{B_0}{M_0} \frac{1}{X} \ln \frac{1}{1-X} \quad (3)$$

The term of $(1/X) \ln (1/(1-X))$ was about 1 at the low conversion, so $k_5/k_3 = 1.018$ could be obtained from Brydon et al. [12]'s result (Table 1). Therefore $f = 0.2868$ was determined for our thermal bulk polymerization.

The crosslinked sites percent in PBD allylic hydrogen was also solved analytically

$$S_x = 2\alpha \left[\frac{1}{\sqrt{1-X}} - 1 \right], \text{ where } \alpha = \frac{\sqrt{3k_1k_4}}{k_2} \left(\frac{k_5B_0}{k_3} \right)^2 \frac{1}{\sqrt{M_0}} \quad (4)$$

and the crosslinked level is drastically increased in the high conversion ($>95\%$) at 190°C (Fig. 2).

CONCLUSIONS

The simple analytic expressions based on the kine-

tic scheme were derived and they predicted the general behaviors of the grafting and crosslinking of PBD during thermal bulk polymerization of HIPS. The effect of temperature on the GE would be offset in terms of the chain transfer ratio so that there was no apparent temperature dependence. The graftability factor (f) and k_5/k_3 were obtained as 0.2868 and 1.018, respectively, from the comparison with experimental data. Crosslinked sites percent of PBD was predicted to show drastically increased at high temperature such as 190°C and at high conversion such as 95%, as expected.

These expressions will be very useful not only for the design and simulation of HIPS process, but also for modeling of styrene-based polymerization process.

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APPENDIX

Derivation of the Graft Fraction, Grafting Efficiency and the Crosslinked Sites

The species mass balance equations arising from the kinetic scheme are

$$\frac{dM}{dt} = -3k_1M^3 - k_2MR - k_2MBR - k_2MB - k_3MR - k_3MBR \quad (A-1)$$

$$\frac{dR}{dt} = 3k_1M^3 + k_3MR - k_4R^2 - k_4RB - k_4BR - k_5B_0R \quad (A-2)$$

$$\frac{dB}{dt} = -k_2MB - k_4B^2 - k_4BR - k_4B - k_5RB_0 + k_5BRB_0 \quad (A-3)$$

$$\frac{dP}{dt} = k_3MR + \frac{1}{2}k_4R^2 + k_5B_0R \quad (A-4)$$

$$\frac{dBR}{dt} = k_2MB - k_3MR - k_4RB - k_4(BR)^2 - k_4BR - k_5B_0BR \quad (A-5)$$

$$\frac{dBP}{dt} = k_3MR - k_4RB - k_4BR + k_5B_0BR \quad (A-6)$$

$$\frac{dB}{dt} = \frac{1}{2}k_4B^2 \quad (A-7)$$

$$\frac{dBPB}{dt} = \frac{1}{2}k_4(BR)^2 + k_4BR \quad (A-8)$$

where

$$R = \sum_{i=1}^{\infty} R_i, BR = \sum_{i=1}^{\infty} BR_i,$$

$$BP = \sum_{i=1}^{\infty} BP_i, \text{ and } BPB = \sum_{i=1}^{\infty} BP_iB.$$

It was needed that the transformation from these into the moments of the distribution functions type. And the moments are defined as

$$U_k = \sum_{n=1}^{\infty} n^k P_n, BU_k = \sum_{n=1}^{\infty} n^k BP_n, BU_0B = \sum_{n=1}^{\infty} n^k BP_n B$$

$$T_k = \sum_{n=1}^{\infty} n^k R_n, BT_k = \sum_{n=1}^{\infty} n^k BR_n$$

From this definition (more detailed procedure was described in reference 1), we can calculate the total amount of monomer polymerized, $U_1 + BU_1 + BU_0B$, and the total amount of monomer grafted, $BU_1 + BU_0B$, and the number crosslinked sites on PBD, $2 \times (BB + BU_0B)$. In the moment distribution function, subscript 0 means a number of event and subscript 1 means the amount that participate in the event. The equations of moment are listed below,

$$\frac{dM}{dt} = -3k_1M^3 - k_2M(T_0 + BT_0 + B) - k_3M(T_0 + BT_0) \quad (A-9)$$

$$\frac{dT_0}{dt} = 3k_1M^3 + k_3M(T_0 + BT_0) - [k_4(T_0 + BT_0 + B) + k_5B_0]T_0 \quad (A-10)$$

$$\frac{dT_1}{dt} = k_2M(T_0 + BT_0) - [k_3M + k_4(T_0 + BT_0 + B) + k_5B_0]T_1 \quad (A-11)$$

$$\frac{dT_2}{dt} = k_2M(2T_1 + T_0) - [k_3M + k_4(T_0 + BT_0 + B) + k_5B_0]T_2 \quad (A-12)$$

$$\frac{dB}{dt} = -[k_2M + k_4(T_0 + BT_0 + B)]B + k_5B_0(T_0 + BT_0) \quad (A-13)$$

$$\frac{dT_0}{dt} = k_2M(B - [k_3M + k_4(T_0 + BT_0 + B) + k_5B_0]BT_0) \quad (A-14)$$

$$\frac{dT_1}{dt} = k_2M(BT_0 - [k_3M + k_4(T_0 + BT_0 + B) + k_5B_0]BT_1) \quad (A-15)$$

$$\frac{dT_2}{dt} = k_2M(2BT_1 + BT_0) - [k_3M + k_4(T_0 + BT_0 + B) + k_5B_0]BT_2 \quad (A-16)$$

$$\frac{dU_0}{dt} = (k_3M + \frac{k_4}{2}T_0 + k_5B_0)T_0 \quad (A-17)$$

$$\frac{dU_1}{dt} = (k_3M + k_4T_0 + k_5B_0)T_1 \quad (A-18)$$

$$\frac{dU_2}{dt} = (k_3M + k_4T_0 + k_5B_0)T_2 + k_4T_1^2 \quad (A-19)$$

$$\frac{dBU_0}{dt} = k_4(BT_0 + B)T_0 + (k_3M + k_5B_0)BT_0 \quad (A-20)$$

$$\begin{aligned} \frac{dBU_1}{dt} &= k_4(BT_0 + B)T_1 + (k_3M + k_4T_0 \\ &\quad + k_5B_0)BT_1 \end{aligned} \quad (A-21)$$

$$\begin{aligned} \frac{dBU_2}{dt} &= k_4(BT_0 + B)T_2 + 2k_4T_1BT_1 + (k_3M + k_4T_0 \\ &\quad + k_5B_0)BT_2 \end{aligned} \quad (A-22)$$

$$\frac{dB}{dt} = \frac{1}{2}k_4B^2 \quad (A-23)$$

$$\frac{dBU_0B}{dt} = k_4\left(\frac{BT_0}{2} + B\right) BT_0 \quad (A-24)$$

$$\frac{dBU_1B}{dt} = k_4(BT_0 + B) BT_1 \quad (A-25)$$

$$\frac{dBU_2B}{dt} = k_4(BT_1)^2 + k_4(BT_0 + B) BT_2 \quad (A-26)$$

Assuming stationary state free radical reactions,

$$\begin{aligned} \frac{dT_0}{dt} &= \frac{dT_1}{dt} = \frac{dT_2}{dt} = \frac{dB}{dt} = \frac{dT_0}{dt} \\ &= \frac{dT_1}{dt} = \frac{dT_2}{dt} = 0 \end{aligned}$$

some of the equations are obtained as

$$3k_1M^3 + k_3M BT_0 - (k_4Y + k_5B_0) T_0 = 0 \quad (A-27)$$

$$k_3M T_0 - (k_3M + k_4Y + k_5B_0) T_1 = 0 \quad (A-28)$$

$$k_2M (2T_1 + T_0) - (k_3M + k_4Y + k_5B_0) T_2 = 0 \quad (A-29)$$

$$- (k_2M + k_4Y) B + k_5B_0(T_0 + BT_0) = 0 \quad (A-30)$$

$$k_2M B - (k_3M + k_4Y + k_5B_0) BT_0 = 0 \quad (A-31)$$

$$k_2M BT_0 - (k_3M + k_4Y + k_5B_0) BT_1 = 0 \quad (A-32)$$

$$k_2M(2BT_1 + BT_0) - (k_3M + k_4Y + k_5B_0) BT_2 = 0 \quad (A-33)$$

, where Y (total radical concentration) = $T_0 + BT_0 + B$
The rate of monomer polymerized is,

$$\frac{d(U_1 + BU_1 + BU_1B)}{dt} = \frac{k_2MY(k_2M + k_4Y)}{k_2M + k_4Y + k_5B_0} \quad (A-34)$$

, where $U_1 + BU_1 + BU_1B = X M_0$, $M = M_0 (1-X)$ and

X =conversion.

To derive the analitic expressions of grafting and crosslinking, some approximations are needed. In the thermal bulk polymerization, the magnitude of k_2M and k_3M are greater than that of k_4Y and k_5B_0 . The expression of monomer grafted as a function of conversion is

$$\begin{aligned} \frac{d(BU_1 + BU_1B)}{d(U_1 + BU_1 + BU_1B)} &= \frac{k_5B_0k_2M}{(k_2M + k_4Y)(k_3M + k_4Y + k_5B_0)} \\ &\approx \frac{k_5B_0}{k_3M} \end{aligned} \quad (A-35)$$

$$BU_1 + BU_1B = \frac{k_5B_0}{k_3M} \ln \frac{1}{(1-X)} \quad (A-36)$$

The graft level as weight percent of PBD, grafting efficiency (GE) is

$$\frac{GE}{100} (\%) = f \frac{M_{St}}{M_{PBD}} \frac{k_5}{k_3} \ln \frac{1}{(1-X)} \quad (A-37)$$

where f is the efficiency of styryl radical chain transfer to allylic hydrogens of PBD in thermal bulk process. In here, we would consider the interference of increased viscosity with the probability of styryl radical transfer to allylic hydrogen of PBD using the graftability factor, f , quantitatively. The graft fraction of PS (GF) is the ratio of the amount of grafted PS to that of polymerized PS (M_0X), so it can be obtained from Eq. (A-34) as bellow

$$GF = \left[\frac{k_5B_0}{k_3} \ln \frac{1}{(1-X)} \right] \left(\frac{1}{M_0X} \right) \quad (A-38)$$

The rate of sites being crosslinked is

$$\begin{aligned} \frac{dS_x}{dt} &= 2 \frac{d(BB + BU_0B)}{dt} \\ &= \frac{k_4(k_5B_0)^2 Y^2 (A + k_2M + k_3M)^2}{(k_2M + A)^2 (k_3M + A)^2} \end{aligned} \quad (A-39)$$

, where $A = k_4Y + k_5B_0$ and the factor 2 is due to the fact that one crosslinked chain takes two sites on the PBD. The expression of crosslinked sites (S_x) as a function of conversion is

$$\frac{1}{M_0} \frac{dS_x}{dX} = \frac{k_4(k_5B_0)^2 Y (k_2 + k_3)^2}{k_2^2 k_3^2 M^3} \quad (A-40)$$

and the value of k_2 is greater than that of k_3 , so we could obtain the simple analytic form as bellow

$$\frac{dS_x}{dX} = \frac{\sqrt{3k_1k_4}}{k_2} \left(\frac{k_5B_0}{k_3} \right)^2 \frac{1}{\sqrt{M_0}} \frac{1}{(1-X)^{2/3}} \quad (A-41)$$

and

$$S_x = 2\alpha \left[\frac{1}{\sqrt{1-X}} - 1 \right]$$

, where $\alpha = \frac{\sqrt{3k_1 k_4}}{k_2} \left(\frac{k_5 B_0}{k_3} \right)^2 \frac{1}{\sqrt{M_0}}$ (A-42)

NOMENCLATURE

M : styrene monomer mole conc.
 M₀ : initial styrene monomer mole conc.
 R_i : styrene radical mole conc.
 BR_i : grafted styrene radical mole conc.
 B₀ : PBD graftable sites (allylic hydrogen) mole conc.
 B : allylic hydrogen abstracted PBD radical mole conc.
 P_i : homo PS mole conc.
 BP_i : grafted PS mole conc.
 BB, BP_B : crosslinked PS mole conc.
 k₁ : initiation rate constant
 k₂ : propagation rate constant
 k₃ : chain transfer constant to homo PS or styrene monomer
 k₄ : termination rate constant
 k₅ : chain transfer constant to grafted PS or graftable sites of PBD
 X : conversion of styrene monomer
 T : reaction temperature [°K]
 GE : grafting efficiency
 f : graftability factor
 GF : grafting fraction

S_x : crosslinked sites
 Y : total radical mole conc.
 M_{ST} : molecular weight of styrene monomer
 M_{PBD} : molecular weight of PBD unit

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