Preparation of Well-Defined Polymers by Polymer-Coupling Reaction. I. A Facile Evaluation of the Extent of Polymer-Coupling Reaction

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Many studies have recently reported on the syntheses of block and graft copolymers by the coupling reaction between two prepolymers.¹ We also have been studying the polymer-coupling reaction by means of either addition^{2a} or substitution.^{2b} In particular, by using a living polymer as one of the prepolymers, we intend to prepare well-defined polymers of the sort shown herein. In these studies of the polymer-coupling reactions, it is desirable to determine the extent of the reaction accurately and easily. In this paper, a method is proposed for direct evaluation of the extent of coupling reaction.

If the number-average molecular weight, $(\bar{M}_n)_R$, of a polymer mixture recovered from any coupling reaction system of A-polymer and B-polymer is measured, the number of polymer molecules, N_R , in the system can be expressed by the equation

$$N_R = \frac{[(\bar{M}_n)_A N_A + (\bar{M}_n)_B N_B]}{(\bar{M}_n)_R} \quad (1)$$

where $(\bar{M}_n)_A$ and $(\bar{M}_n)_B$ are the number-average molecular weights, and N_A and N_B are the initial number of molecules of A-polymer and B-polymer in the system, respectively. N_R can be related to the number of A-polymer molecules which have coupled with B-polymer, n_A , in a simple relation as shown in Table I. Therefore, the extent of coupling of A-polymer, n_A/N_A , can be calculated by the equation

$$\frac{n_A}{N_A} = \left\{ \frac{1 + \nu - [(\bar{M}_n)_A + (\bar{M}_n)_B \nu]}{(\bar{M}_n)_R} \right\} f \quad (2)$$

where ν stands for N_B/N_A , and f is equal to unity in the case of monofunctional A-polymer, but for bifunctional A-polymer f is given in Table II. In the equations, N_A , N_B , or n_A may be expressed in moles.

In the proposed method, the recovered polymer mixture needs no further fractionation or separation for the evaluation of the extent of coupling, but its number-average molecular weight should be measured accurately. It is not necessary to consider the kind of solvent for the extraction of products, the contamination of products by uncoupled precursor molecules, the distribution of precursor molecules on coupler molecules, etc. However, the extent of any side reaction should be evaluated in advance, if it may change the number of polymer molecules for the scission of the main chains or coupling of the prepolymers of the same kinds during the desired coupling reaction.

Prior to the application of this method to a polymer-coupling reaction, it was tested by a blend of two inert polymers which was chosen as an extreme example having no coupling reaction in the system, where the values of n_A/N_A were found equal to zero within experimental error, as shown in Table III.

This method will be suitable for study of the coupling reaction in detail, especially for the

Table I. Type of resultant polymers and the number of polymer molecules in the system after the coupling reaction between A-polymer and B-polymer

No.	Type of resultant coupled polymer	Nature of reactant		No. of molecules of A-polymer that coupled with B-polymer	No. of polymer molecules, N_R , in the system after the reaction
		A-polymer	B-polymer		
1	Block	AB	Monofunc ^a	n_A	$N_A + N_B - n_A^b$
		ABA	Monofunc		
		BAB	Bifunc	$n_A \left\{ \frac{n_A(\chi_b)_A}{n_A[1 - (\chi_b)_A]} \right\}^e$	$N_A + N_B - n_A[1 + (\chi_b)_A]$
		ABAB... ^d	Bifunc		
2	Ring-shaped	$\left(\text{---}(\text{AB})\text{---} \right)_n^f$	Bifunc	n_A	$N_A + N_B - n_A(2 - 1/\bar{n})^g$
3	Graft	A_nB	Monofunc	n_A	$N_A + N_B - n_A$
4	Star-shaped	A_nB	Monofunc		
5	Cross-linked	A_nB_n	Bifunc	$n_A \left\{ \frac{n_A(\chi_{\text{inter}})_A}{n_A[1 - (\chi_{\text{inter}})_A]} \right\}^j$	$N_A + N_B - n_A[1 + (\chi_{\text{inter}})_A]$

^a Monofunctional.^b N_A , total number of A-polymer molecules; N_B , total number of B-polymer molecules.^c Bifunctional.^d Obtained when no backbiting reaction takes place.^e $(\chi_b)_A$, fraction of number of A-polymer molecules coupled bifunctionally.^f Obtained when all molecules react bifunctionally.^g $\bar{n}$, average number of AB sequence in ring polymers.^h Multifunctional and linear.ⁱ Multifunctional low-molecular-weight compound.^j $(\chi_{\text{inter}})_A$, fraction of number of A-polymer molecules coupled intermolecularly.**Table II.** Type of resultant polymers and factors (f) of eq 2

No.	Type of resultant coupled polymer	f	Remarks
1	Block AB, ABA	1	$n_A = n_B$ for AB case and $n_A = n_B[1 + (\chi_b)_B]$ for ABA case. ABA-type products may contain some AB-type molecules. If n_A can be found, a number of BAB polymer molecules or the average number of AB sequence in ABAB... polymer is determined.
	BAB, ABAB...	$1/[1 + (\chi_b)_A]$	
2	Ring-shaped $\left(\text{---}(\text{AB})\text{---} \right)_n$	$1/(2 - 1/\bar{n})$	The number of coupled branches of B-polymer may be calculated from n_A/N_A if all molecules of A-polymer are assumed to couple with every B-polymer molecule evenly. f is equal to unity even if the coupling takes place unevenly. The same remark as for the graft case. The value of $(\bar{M}_n)_{BV}$ may be negligibly small compared with $(\bar{M}_n)_A$. Membrane osmometry may be difficult unless every B-molecule has at least one coupled branch as B is generally a low-molecular-weight compound.
3	Graft A_nB	1	
4	Star-shaped A_nB	1	
5	Cross-linked A_nB_n	$1/[1 + (\chi_{\text{inter}})_A]$	This factor may be effective ^a at an early stage in the reaction where $(\bar{M}_n)_R$ can be measured.

^a If n_A/N_A can be guessed from model reactions or otherwise, $(\chi_b)_A$, $\bar{n}$, $(\chi_{\text{inter}})_A$, or $(\chi_{\text{intra}}) (= 1 - (\chi_{\text{inter}})_A)$ can be estimated.

Table III. Application of eq 2 to the case of inert blends

Inert blend				$\nu, N_B/N_A$	$(\bar{M}_n)_R^c \times 10^{-4}$		n_A/N_A^d
A-polymer ^a		B-polymer ^b			Obsd ^g	Calcd ^h	
mg	mol ^e	mg	mol ^f				
9.5	3.85×10^{-7}	80.4	1.61×10^{-7}	4.18×10^{-1}	15.9	16.4	-0.05
40.4	1.64×10^{-6}	41.3	8.29×10^{-8}	5.05×10^{-2}	4.72	4.75	-0.01
79.8	3.23×10^{-6}	10.2	2.05×10^{-8}	6.35×10^{-3}	2.83	2.77	+0.02

^a Monodisperse polystyrene, $(\bar{M}_n)_A = 2.47 \times 10^4$.^b Monodisperse polystyrene, $(\bar{M}_n)_B = 49.8 \times 10^4$.^c Number-average molecular weight of the blends.^d Calculated from the value of $1 + \nu - [(\bar{M}_n)_A + (\bar{M}_n)_B \nu] / (\bar{M}_n)_R$ by using $(\bar{M}_n)_R$ observed. The positive or negative small value is the experimental error.^{e, f} Obtained by dividing the weight of A- or B-polymer by $(\bar{M}_n)_A$ or $(\bar{M}_n)_B$, and each value equals N_A/k or N_B/k , respectively, where k denotes Avogadro number.^g Determined by membrane osmometry.^h Calculated by the equation $n_A/N_A = 1 + \nu - [(\bar{M}_n)_A + (\bar{M}_n)_B \nu] / (\bar{M}_n)_R$, where $n_A = 0$.Table IV. Comparison with other methods^a

Method	Extent of coupling of living PST, %				
	Experiment no.				
	SOL-1	SOL-5	SOL-23	SOK-2	K-3
GPC	58.7	33.1	76.5	59.7	77.7
Turbidimetric titration	53	31	—	—	—
Fractional precipitation	—	{36.3 ^b 18.0 ^c }	—	—	78.7 ^b
This method (eq 2)	61.5	39.3	80.8	61.0	79.5

^a Procedure for the methods and the reaction conditions of coupling reactions are given in ref 2a for experiments SOL-1, SOL-5, SOL-23, and SOK-2 and in ref 2b for K-3.^b From the weight of fractionated graft polymer.^c From the number-average molecular weight of fractionated graft polymer.

investigation of the effect of various conditions on the reaction, as it may provide accuracy and facility in comparison with conventional methods which have been used until now such as (1) solvent extraction,^{3a} (2) fractional precipitation,^{3b}

(3) determination of the functional group remained,^{3c} (4) turbidimetric titration,^{3d} or (5) gel permeation chromatography.^{3e}

The method was applied to the coupling reaction of living polystyrene with poly(*p*-vinylstyrene oxide)^{2a} or poly(chloromethylstyrene)^{2b} successfully, giving results in good agreement with other methods as shown in Table IV.

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