Rheological Properties of the Solutions of Incompatible Polymer Blends

Jeong In Sohn and Taikyue Ree[†]

Department of Chemistry, Korea Advanced Institute of Science and Technology, P.O.Box 150, Chongyangni, Seoul 131, Korea (*Received July 27, 1981*)

A blend polymeric system composed of poly(methyl methacrylate) (PMMA or PM) and polystyrene (PS) dissolved in chlorofolm was rheologically studied. The viscosities η_{bl} of the blend system with various blending ratios χ changing from zero (pure PS solution) to unity (pure PMMA solution) were measured at 25 °C as a function of shear rates $\dot{s}$ by using a Couette type viscometer. η_{bl} at a given $\dot{s}$ decreased exponentially with χ reaching asymptotic constant value of η_{bl} ; η_{bl} at a given χ is greater at a smaller $\dot{s}$. These results are explained by using Ree–Erying's theory of viscosity, $\eta_{bl}=(x_1\beta_1/\alpha_1)_{b,}+(x_2\beta_2/\alpha_2)_{bl}\,[\sinh^{-1}\beta_2(bl)\,\dot{s}]/\beta_2(bl)\dot{s}$. The Gibbs activation energy $\Delta G_i^{\ast}$ ($i=2$ for non–Newtonian units) entering into the intrinsic relaxation time β_i is represented by a linear combination $\Delta G_i^{\ast}(bl)=\chi\Delta G^{\ast}_{i\mathrm{PM}}+(1-\chi)\Delta G^{\ast}_{i\mathrm{PS}}$;the intrinsic shear modulus$[\alpha_i]^{-1}$ is also represented by $[\alpha_i(\mathrm{bl})]^{-1}=\chi[\alpha_{i\mathrm{PM}}]^{-1}+(1-\chi)\,[\alpha_{i\mathrm{PS}}]^{-1}$ and the fraction of area on a shear surface occupied by the ith flow units $x_i(bl)$ is similarly represented, *i.e.*, $x_i(bl)=\chi x_{i\mathrm{PM}}+(1-\chi)x_{i\mathrm{PS}}$. By using these ideas the Ree–Eyring equation was rewritten which explained the experimental results statisfactorily.

Introduction

Ree–Eyring's equation for viscous flow was applied to various systems. Polymeric solids and solutions,[1] suspension systems,[2] metals and alloys[3] are well explained by the theory. In this paper, we tested the applicability of the theory to a emulsion system which is composed of polystyrene(PS) and poly(methyl methacrylate) (PMMA or PM) in a cosolvent, chloroform.

Most of polymer pairs are incompatible because of their negligible entropy of mixing. And viscosity profiles of polymer blends in melt do not obey and simple "law of additivity" in terms of blending ratios, but have maxima or minima in the curves of viscosity *vs.* blending ratio.[4] The viscosity profiles of two phase polymer–melt systems vary not only by shear rates and temperatures but also by molecular weights of polymer samples and blending methods[5] significantly. And morphology of the flow system has also strong effects on the viscosity.[5] But in ternary systems which contain a cosolvent, blending methods and morphology factors are eliminatable. Krause reviewed the compatibility of ternary systems.[6] Our system of polystyrene/poly(methyl methacrylate) in chloroform is a incompatible one.

Theory

1. The Ree–Eyring Equation of Viscosity. According to the generalized theory of viscosity,[1] η can be expressed by Eq. (1),

$$\eta=\sum_i\frac{x_i\beta_i}{\alpha_i}\;\frac{\sinh^{-1}\beta_i\,\dot{s}}{\beta_i\,\dot{s}}\tag{1}$$

where x_i is the fraction of area occupied on a shear surface by the ith flow unit; $\dot{s}$ is shear rate; $\alpha_i=(\lambda\lambda_2\lambda_3/2\mathrm{kT})_i$ and $\beta_i=(2k'\lambda/\lambda_1)_i^{-1}$, the quantities $(\alpha_i)^{-1}$ and β_i being proportional to the shear modulus and relaxation time of the ith flow unit, respectively, λ, λ_1, λ_2. λ_3 are the molecular parameters appearing in the Eyring theory of flow,[7] k' the rate constant (jumping frequency) of a flow unit, and the subscript i outside the parenthesese indicates that the indside quantities belong to the ith flow unit.

Two types of flow units are assumed in this study, *i.e.*, $i=1$ and 2. Generally β_1 is very small, and the following relation holds

$$\frac{\sinh^{-1}\beta_1\,\dot{s}}{\beta_1\,\dot{s}}\longrightarrow 1\ \text{if}\ \beta_1\,\dot{s}\ll 1$$

$$\eta=\frac{x_1\beta_1}{\alpha_1}+\frac{x_2\beta_2}{\alpha_2}\;\frac{\sinh^{-1}\beta_2\,\dot{s}}{\beta_2\,\dot{s}}\tag{2}$$

i.e., the first type of flow units ($i=1$) acts as a Newtonian type whereas the second type acts as a non–Newtonian. In the first type, the solvent flow units are also included.

Generally, β_i is represented by the following equtiion:

$$\begin{aligned}\beta_i&=1/\left(\frac{\lambda}{\lambda_1}2\,k'\right)_i\\&=1/\left(\frac{\lambda}{\lambda_1}\right)_i 2\,\frac{kT}{h}e^{-\Delta G_i^{\ast}/RT}\end{aligned}\tag{3}$$

where the rate constant k_i' is substituted by the absolute reaction rate constant.

2. Application of Ree–Eyring Equation to a Blend Polymer Solution.

Let η_{bl} be the viscosity of the blend polymer solution which is composed of polystyrene (PS) and poly(methyl methacrylate) (PMMA or PM) in chloroform. In accordance with Eq. (2), η_{bl} is expressed by the following equation:

$$\eta_{bl}=\left(\frac{x_1\beta_1}{\alpha_1}\right)_{bl}+\left(\frac{x_2\beta_2}{\alpha_2}\right)_{bl}\;\frac{\sinh^{-1}\beta_2(bl)\dot{s}}{\beta_2(bl)\dot{s}}\tag{4}$$

That is, the blend system is also composed of Newtonian and non–Newtonian type flow units which are represented by the subscripts 1 and 2, respectively. We consider first the intrinsic relaxation time $\beta_2(bl)$ of the blend system.

Intrinsic Relaxation Time $\beta_2(bl)$ of the Non–Newtonian Blend Flow Units. The $\beta_2(bl)$ is given by an equation similar to Eq. (3), *i.e.*,

$$\beta_2(bl)=1/\left(\frac{\lambda}{\lambda_1}\right)_{bl}\frac{2kT}{h}\exp\left[\frac{-\Delta G_2^{\ast}(bl)}{RT}\right]\tag{5}$$

The activation free energy $\Delta G_2^{\ast}(bl)$ of the blend system is assumed to be given by the following equation.

$$\Delta G_2^{\ddagger}(bl)=\chi\Delta G_{2PM}^{\ddagger}+(1-\chi)\Delta G_{2PS}^{\ddagger} \tag{6}$$

where χ is the blending ratio [$\chi=0$, pure polystyrene solution, $\chi=1$, pure poly(methyl methacrylate) solution], $\Delta G_{2PM}^{\ddagger}$ and $G_{2PS}^{\ddagger}$ represent the activation free energies in solutions of pure **PMMA** and pure **PS** in chloroform, respectively. The relaxation times β_{2PM} and β_{2PS} of the two pure solution systems, are given by similar equations as Eq. (3), *i.e.*,

$$\beta_{2PM}=1/\left[\left(\frac{\lambda}{\lambda_1}\right)_2\frac{2kT}{h}\exp\left(-\frac{\Delta G_2^{\ddagger}}{RT}\right)\right]_{PM} \tag{7}$$

and

$$\beta_{2PS}=1/\left[\left(\frac{\lambda}{\lambda_1}\right)_2\frac{2kT}{h}\exp\left(\frac{-\Delta G_2^{\ddagger}}{RT}\right)\right]_{PS} \tag{8}$$

If the approximation, $(\lambda/\lambda_1)_{2PM}\simeq(\lambda/\lambda_1)_{2PS}$ is made for simplicity, Eqs. (7) and (8) yield, respectively,

$$\beta_{2PM}=C\exp\frac{\Delta G_{2\ PM}^{\ddagger}}{RT} \tag{9}$$

and

$$\beta_{2PS}=C\exp\frac{\Delta G_{2\ PS}^{\ddagger}}{RT} \tag{10}$$

where $C=h/2kT(\lambda/\lambda_1)_2$

We introduce Eq. (6) into (5), then the following results:

$$\beta_2=(bl)=C\exp\frac{[\chi\Delta G_{2PM}^{\ddagger}+(1-\chi)\Delta G_{2PS}^{\ddagger}]}{RT} \tag{11}$$

where the approximation, $h/2kT(\lambda/\lambda_1)_{2,\,bl}\simeq$ C, was made. By comparing Eqs. (9), (10)and (11), one obtains,

$$\beta_2(bl)=\beta_{2PM}^{\chi}\,\beta_{2PS}^{1-\chi} \tag{12}$$

By using Eq. (12), the $\beta_2(bl)$ values at any χ can be calculated in terms β_{2PM} and β_{2PS}, the latter quantitis being experimentally obtainable from flow curves for pure **PMMA** and **PS** solutions

Parameter$(x_2/\alpha_2)_{bl}$ *for a Blend System.* In this parameter, $1/\alpha_2$ is the intrinsic shear modulus of flow unit 2, and $[\alpha_2(bl)]^{-1}$ is also expressed by a linear combination as follows:

$$[\alpha_2(bl)]^{-1}=\chi[\alpha_{2PM}]^{-1}+(1-\chi)[\alpha_{2PS}]^{-1} \tag{13}$$

The area fraction $x_2(bl)$ occupied by flow units 2 in the blend system is similarly expressed by

$$x_2(bl)=\chi x_{2PM}+(1-\chi)x_{2PS} \tag{14}$$

By combining Eqs. (13) and (14), one obtains:

$$\left(\frac{x_2}{\alpha_2}\right)_{bl}=a\chi^2+b\chi+c \tag{15}$$

Non-Newtonian Viscosity Term $\eta_2(bl)$. The term of non-Newtonian viscosity, $\eta_2(bl)$, in Eq. (4) is expressed by using Eqs. (12) and (15) as

$$\eta_2(bl)=(a\chi^2+b\chi+c)\beta_{2PM}^{\chi}\,\beta_{2PS}^{1-\chi}\times\frac{\sinh^{-1}\beta_{2PM}^{\chi}\,\beta_{2\ PS}^{1-\chi}\,\dot{s}}{\beta_{2PM}^{\chi}\,\beta_{2P}^{1-\chi}\,\dot{s}} \tag{16}$$

From Eq. (16), one notes that $\chi\rightarrow0$, $\eta_2(bl)$ becomes η_{2PS}, *i.e.*,

$$\eta_{2PS}=c\,\beta_{2PS}\frac{\sinh^{-1}\beta_{2PS}\,\dot{s}}{\beta_{2PS}\,\dot{s}} \tag{17}$$

From Eq. (2), the η_{2PS} is experssed by

$$\eta_{2PS}=\left(\frac{x_2\beta_2}{\alpha_2}\right)_{PS}\frac{\sinh^{-1}\beta_{2PS}\,\dot{s}}{\beta_{2PS}\,\dot{s}} \tag{18}$$

By comparing Eqs. (17) and (18), one obtains

$$c=(x_2/\alpha_2)_{PS} \tag{19a}$$

thus c is obtained from (x_2/α_2) which is available from a flow curve of a pure PS solution.

On the other side, at $\chi=1$, one obtaines from Eq. (16) the following relation:

$$\eta_2(bl)=\eta_{2PM}=(a+b+c)\beta_{2PM}\frac{\sinh^{-1}\beta_{2PM}\,\dot{s}}{\beta_{2PM}\,\dot{s}}$$

which yields the relation,

$$a+b+c=\left(\frac{x_2}{\alpha_2}\right)_{PM}$$

i.e.,

$$a+b=\left(\frac{x_2}{\alpha_2}\right)_{PM}-\left(\frac{x_2}{\alpha_2}\right)_{PS} \tag{19b}$$

Newtonian Viscosity Term. In the Newtonian viscosity term $x_1\beta_1/\alpha_1$ in Eq. (2), the β_1 factor is unseparable from x_1/α_1 while β_2 is separanle from x_2/α_2 in the non-Newtonian term. One may, however, assume that an equation similar to Eq. (11) will be applied to β_1 in a blend system. Thus,

$$\beta_1(bl)=C'\exp\chi[\Delta G_{1PM}^{\ddagger}-\Delta G_{1PS}^{\ddagger}]/RT$$

the difference quantity in the bracket will be negative since the relation, $\Delta G_{PM}^{\ddagger}<\Delta G_{PS}^{\ddagger}$, generally holds, *i.e.*,

$$\beta_1(bl)\equiv C'\exp\left[-\frac{\chi|\delta\Delta G_1^{\ddagger}|}{RT}\right] \tag{20}$$

The quantity $(x_1/\alpha_1)_{bl}$ may also be expressed by an equation similar to Eq. (15), *i.e.*

$$(x_1/\alpha_1)_{bl}=a'\chi^2+b'\chi+c' \tag{21}$$

By combining Eqs. (20) and (21), one obtains for the Newtonian term the following equation:

$$\left(\frac{x_1\beta_1}{\alpha_1}\right)_{bl}=(a'\chi^2+b'\chi+c')\exp\left[\frac{-\chi|G_1^{\ddagger}|}{RT}\right] \tag{22}$$

where the constant C' in Eq. (20) is absorbed into the coefficients a', b' and c'. If $\chi\rightarrow0$, Eq. (22) becomes

$$\left(\frac{x_1\beta_1}{\alpha_1}\right)_{bl}=\left(\frac{x_1\beta_1}{\alpha_1}\right)_{PS}=c' \tag{23}$$

thus, c' is obtainable from a flow curve of a pure PS solution. For the determination of a and b in Eq. (16) and a' and b' in Eq. (22), reference is made to a later part.

Esperimental

1. Sample Preparation

Polystyrene. Commercially available general-purpose polystyrene (PS) (Han Nam Chemical Co.) is used without further treatment.

Poly(methyl methacrylate). Poly(methyl methacrylate) (PMMA or PM) was polymerized in benzene solution using benzoylperoxide as an initiator.

2. Moecular Weight Measurment

A Cannon Fenske capillary viscometer was used to obtain the intrinsic viscosity. The molecular weights of sample PS and PMMA polymers were 87,000 and 38,000, respectively.

3. Measurments of Viscosities

The solutes of 36 g were added in 90 m*l* of chloroform (Wako, EP) irrespective of the blending ratios. A Coutte type rotational viscometer was used, and by an X–Y recorder, the curves of shear stress f were obtained at 25 °C. Viscosities of eleven solutions of blend samples of PS and PMMA changing in the blending ratios from zero (pure PS solution) to unity (pure PMMA solution) were measured at various shear rates.

Results

Flow Curves and Viscosities. The profile of flow curve of $\dot{s}$ *vs.* f for a blend sample was typically non-Newtonian, *i.e.*, it is not a straight line, but bends upward. The viscosity η is given by $f/\dot{s}$, and corresponds to the reciprocal of the slope of the curve at a point. Viscosities η_{bl} of the samples of various blending ratios χ were measured at three different shear rates, and are plotted againt χ in Figure 1. We see the decrease in the viscosities with increasing shear rates. This is also a characteristic of non-Newtonian flow. With increasing χ, the viscosity decreases at a given $\dot{s}$, *i.e.*, pure PMMA solution is lower than pure PS solution in viscosity.

We also note that η reaches a nearly constant value above 30 wt% PMMA content for each $\dot{s}$.

Determination of Flow Parameters. Because of the nature of the inverse hyperbolic sine function, $(\sinh^{-1}\beta_2\dot{s})/\beta_2\dot{s}$ approaches zero as $1/\dot{s}$ approaches zero. We can obtain the values of $x_1\beta_1/\alpha_1$ in Eq.(2) by plotting η *vs.* $1/\dot{s}$ on the intercept of the curve at $(1/\dot{s})=0$. We denote this quantity by $\eta_\infty(=x_1\beta_1/\alpha_1)$ which is a Newtonian type viscosity $(i=1)$.

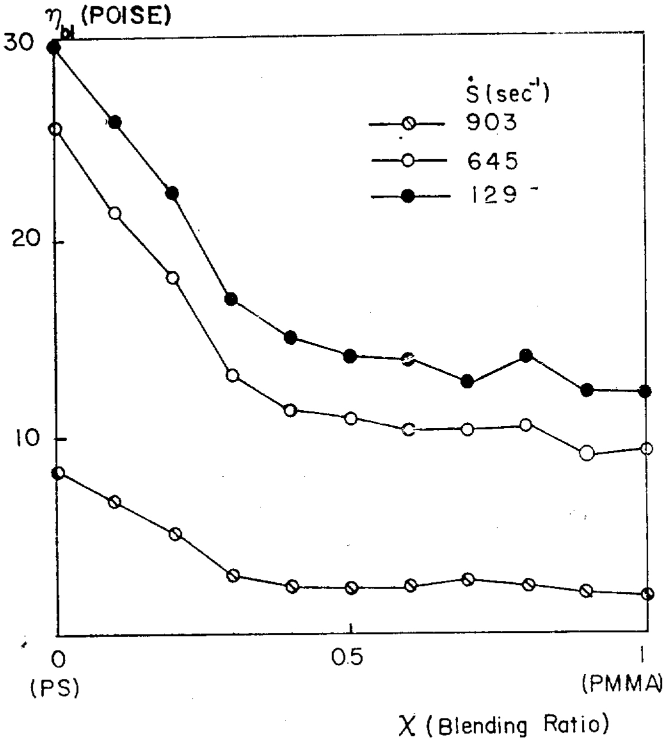

Figure 1. Viscosity η_{bl} of blend solutions at three different shear rates $\dot{s}$ *vs.* blending ratio χ. $\chi=0$ for pure PS solution, $\chi=1$ for pure PMMA solution.

Table 1: Values of Parameters in the Ree–Eyring Theory

χ^a	$\frac{x_1\beta_1{}^b}{\alpha_1}(=\eta_\infty)$	$\frac{x_2\beta_2{}^b}{\alpha_2}$	$\beta_2{}^c\times10^3$	$\frac{x_2{}^d}{\alpha_2}\times10^{-3}$
0	11.8	19.6	9.11	2.15
0.1	8.1	20.8	7.22	2.88
0.2	7.0	13.2	6.91	1.91
0.3	6.0	5.6	4.99	1.12
0.4	6.9	4.5	5.38	0.84
0.5	5.8	3.6	4.83	0.75
0.6	5.5	3.7	4.09	0.91
0.7	6.0	2.5	3.33	0.75
0.8	6.0	2.9	3.35	0.85
0.9	5.1	2.3	2.82	0.81
1.0	4.7	2.7	2.51	1.08

[a] Blending ratio $\chi=0$ for pure PS solution, $\chi=1$ for pure PMMA solution. [b] In the determination of the parameters, an extrapolation process is involved. (See the text.) The unit of the parameter is poise. [c] Because of a small fluctuation of the value due to $\dot{s}$, an average was taken. The unit is sec. *d.* The unit is dyne/cm².

The parameters x_2/α_2 and β_2 in the non-Newtonian type are obtained by applying the Ree–Eyring equation to the flow curve. The principle is as follows: (i) the factor $(\sinh^{-1}\beta_2\dot{s})/\beta_2\dot{s}$ approaches to unity as $\dot{s}\rightarrow0$; (ii) according to Eq. (2); $\eta-\eta_\infty=(x_2\beta_2/\alpha_2)(\sinh^{-1}\beta_2\dot{s})/\beta_2\dot{s}$;(iii) thus $(x_2\beta_2/\alpha_2)$ is obtained by polotting $\eta-\eta_\infty$ *vs.* $\dot{s}$ and by extrapolating the curve to $\dot{s}=0$, *i.e.*, the intercept on the $(\eta-\eta_\infty)$ axis yields $x_2\beta_2/\alpha_2$; (iv) then β_2 is obtained by the following way: by using the value of $x_2\beta_2/\alpha_2$ just obtained, the value of $(\eta-\eta_\infty)/[x_2\beta_2/\alpha_2]$ is calculated which equals $(\sinh^{-1}\beta_2\dot{s})/\beta_2\dot{s}$, *i.e.*,

$$\frac{(\eta-\eta_\infty)}{(x_2\beta_2/\alpha_2)}=\frac{\sinh^{-1}\beta_2\dot{s}}{\beta_2\dot{s}}$$

the β_2 satisfying the above relation is easily obtained since all the equatities appearing in the relation are known except for β_2.

All the parametric values obtained by the above method of analysis are tabulated in Table 1 where the parameters are represented as a function of χ. In Table 1, the data of pure PS solution $(\chi=0)$ and of pure PMMA solution $(\chi=1)$ are also found.

Relaxation Time $\beta_2(bl)$. From Eq. (12), we obtain,

$$\begin{aligned}\ln\beta_2(bl)&=\chi\ln\beta_{2PM}+(1-\chi)\ln\beta_{2PS}\\&=\chi\ln\frac{\beta_{2PM}}{\beta_{2PS}}+\ln\beta_{2PS}\end{aligned}\tag{24}$$

In Figure 2, the values of $\ln\beta_2(bl)$ are plotted against χ, the data are taken from Table 1. The straight line in Figure 2 is the plot of Eq. (24), *i.e.*, the slope of the straight line is $\ln[\beta_{2PM}/\beta_{2PS}]$, and the intercept at $\chi=0$ is $\ln\beta_{2PS}$. One notes from Figure 2, that the agreement between theory and experiment is very good.

Parameter $(x_2/\alpha_2)_{bl}$. In Figure 3, the parameters $(x_2/\alpha_2)_{bl}$ are plotted against χ, the data are from Table 1. The full curve was calculated from Eq. (15) which seems to fit the experimental points satisfactorily. The values of constants, *a*,*b* and *c* in Eq. (15) were obatained by using Eqs. (19a) and (19b), where $a=2.70\times10^3$ was chosen. Thus, b was calculated

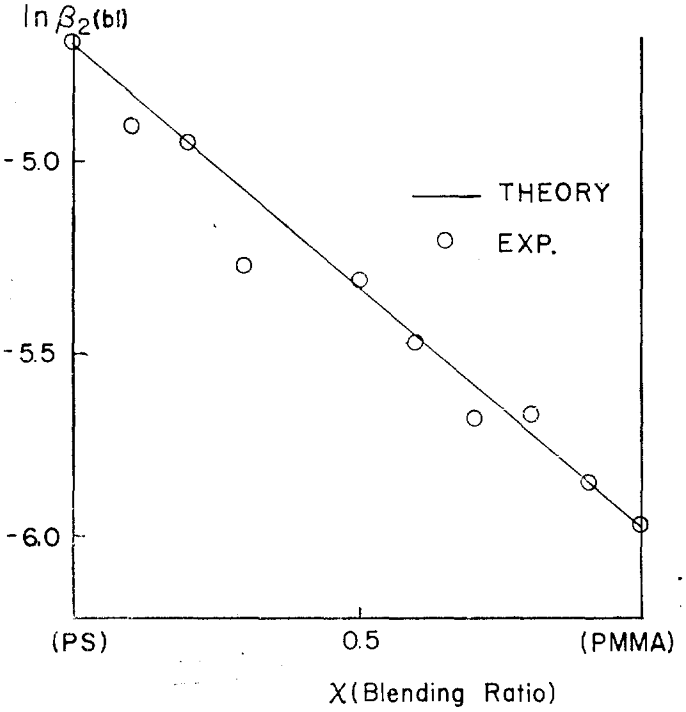

Figure 2. ln $\beta_2(bl)$ *vs.* χ. The $\beta_2(bl)$ is the intrinsic relaxation time of a non-Newtonian flow unit in blend solution. The straight line is represented by Eq. (24). $\chi=0$ for pure PS solution, $\chi=1$ for pure PMMA solution.

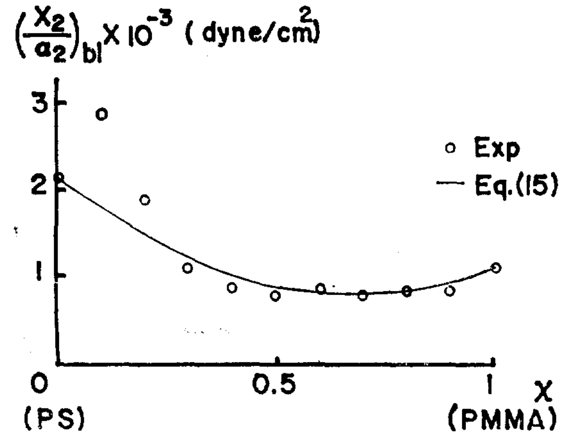

Figure 3. Parameter $(x_2/\alpha_2)_{bl}$ *vs.* χ. The $(x_2/\alpha_2)_{bl}$ is the parameter x_2/α_2 for a non-Newtonian unit in blend solution, the full curve is represented by Eq. (15), where the values of a, b and c are 2.70, -3.77 and 2.15 in units of 10^3 dyne/cm^2, respectively. $\chi=0$ for pure PS solution, $\chi=1$ for pure PMMA solution.

from Eq. (19b) by using the values of $(x_2/\alpha_2)_{PM}$ $(=1.08\times10^3)$ and $(x_2/\alpha_2)_{PS}$ $(=2.15\times10^3)$, *i.e.*,$b=-3.77\times10^3$. According to Eq. (19a), $c=(x_2/\alpha_2)_{PS}=2.15\times10^3$. The values of $(x_2/\alpha_2)_{PM}$ and $(x_2/\alpha_2)_{PS}$ were taken from Table 1.

Newtonian Term $(x_1\beta_1/\alpha_1)_{bl}$. This term is also expressed as $\eta_\infty(bl)$as previously mentioned. In Figure4 are shown ln η_∞ (bl) *vs.* χ, the data being taken from Table 1. The full curve is obtained from Eq. (22), where the value of $[|\delta\Delta G_1^\ddagger|]$/RT was found to be 0.4.

From Eq. (22), one notes that if $\chi\rightarrow0$, $(x_1\beta_1/\alpha_1)_{bl}$ becomes $(x_1\beta_1/\alpha_1)_{PS}(=11.8)$ which equals c' as previously mentioned. [See Eq.(23)]. One also notes that if $\chi\rightarrow1$, $(x_1\beta_1/\alpha_1)_{bl}$ becomes $(x_1\beta_1/\alpha_1)_{PM}$ which equals $(a'+b'+c')$ exp $[-|\delta\Delta G^\ddagger|/RT]$, *i.e.*,

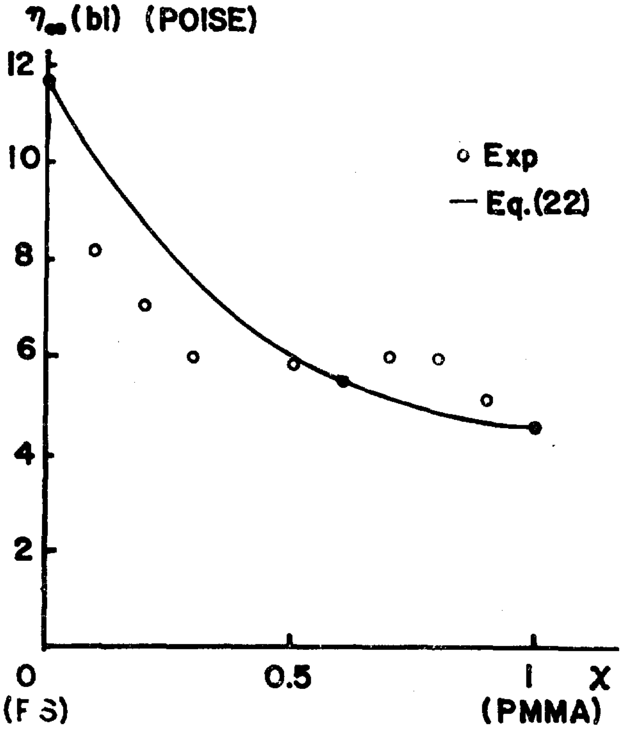

Figure 4. $\eta_\infty(bl)$ *vs.* χ. The $\eta_\infty(bl)$ represents $(x_1\beta_1/\alpha_1)_{bl}$, *i.e.*, the Newtonian viscosity for blend solution. The full curve is represented by Eq. (22), where the values of a', b', c' and $|\delta\Delta G_1^\ddagger|/RT$ are 8.3, -13.1, 11.8 and 0.4, respectively.

$$(a'+b'+c')=\left(\frac{x_1\beta_1}{\alpha_1}\right)_{PM}\exp\left(\frac{-|\delta\Delta G_1^\ddagger|}{RT}\right)$$

or

$$a'+b'=\left(\frac{x_1\beta_1}{\alpha_1}\right)_{PM}\exp\left(\frac{-|\delta\Delta G_1^\ddagger|}{RT}\right)-\left(\frac{x_1\beta_1}{\alpha_1}\right)_{PS} \quad (25)$$

where a' is found to be 8.3. By substituting the known values of a' and $[|\delta\Delta G_1^\ddagger|]/RT$, and by using the values of$(x_1\beta_1/\alpha_1)_{PM}$ and $(x_1\beta_1/\alpha_1)_{PS}$ in Table 1, b' was calculated as -13.1 from Eq. (25).

Calculation of Viscosities for Blend Systems and Discnssions

1. Curves of η *vs.* $\dot{s}$.

By substuting the known values of a', b', $(x_1\beta_1/\alpha_1)_{PS}$ and $[|\delta\Delta G_1^\ddagger|]$/RT to the Newtonian term$(x_1\beta_1/\alpha_1)_{bl}$ in Eq. (22), and by introducing, a,b, $(x_2\alpha_2)_{PS}$, β_{2PM} and β_{2PS} to the non-Newtonian term $\eta_2(bl)$ in Eq. (16), we obtain $\eta_{bl}=[\eta_\infty(bl)+\eta_2(bl)]$ as follows:

$$\eta_{bl}=(8.3\chi^2-13.1\chi+11.8)\exp(-0.4\chi)$$
$$+10^3(2.70\chi^2-3.77\chi+2.15)\beta_{2PM}^{\chi}\beta_{2PS}^{1-\chi}\frac{\sinh^{-1}\beta_{2PM}^{\chi}\beta_{2PS}^{1-\chi}\dot{s}}{\beta_{2PM}^{\chi}\beta_{2PS}^{1-\chi}\dot{s}} \quad (26)$$

where β_{2PM} and β_{2PS} are 9.11×10^{-3} and 2.51×10^{-3} sec, respectively. By using Eq. (26),the viscosities η_{bl} were calculated at various blending ratios χ as a function shear rate $\dot{s}$. The results are shown in Figures 5a and 5b. The agreement between theory and experiment is generally good except for the

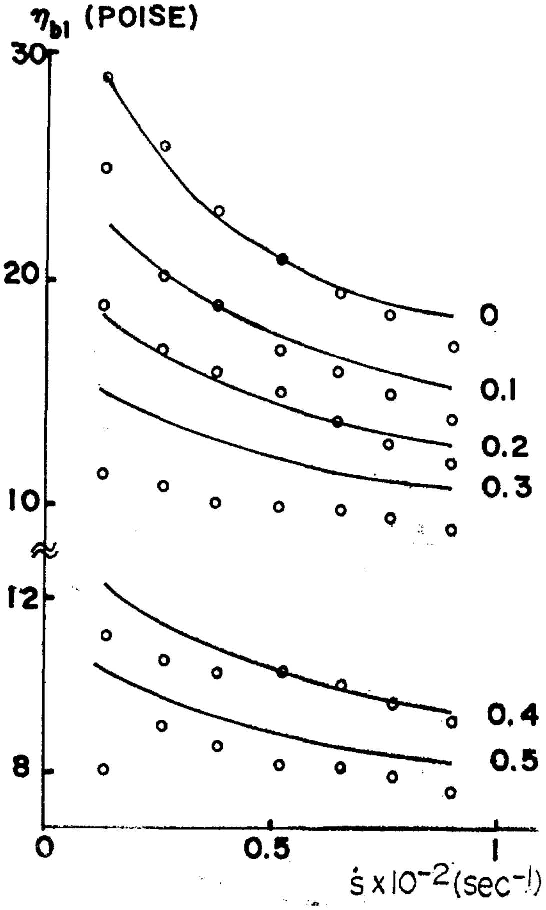

Figure 5a. Viscosity η_{bl} for blend solution at various shear rates ṡ and blending ratios from $\chi=0$ to $\chi=0.5$. The full curves are calculated from Eq. (26). The blending ratios are shown on the curves. $\chi=0$ for pure PS solution, $\chi=1$ for pure PMMA solution.

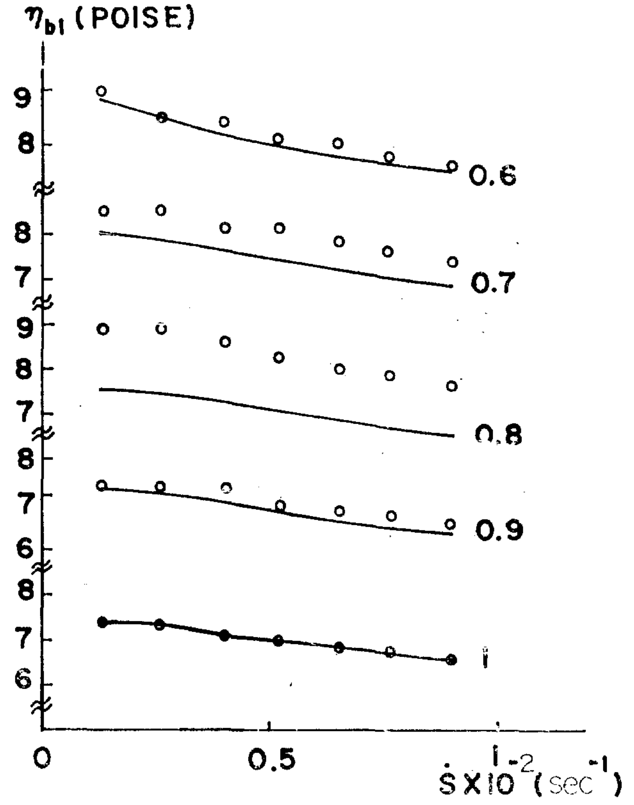

Figure 5b. Viscosities η_{bl} for blend solution at various shear rates ṡ and blending ratios from $\chi=0.6$ to $\chi=1$. The full curves are claculated from Eq. (26). The blending ratios are shown on the cruves. $\chi=0$ for pure PS solution, $\chi=1$ for pure PMMA solution.

cases of $\chi=0.3$ and $\chi=0.8$. It is regarded that the discrepancies appeared at these χ's may be due to some systematic experimental errors.

2. Discussions

Flat Portion on a Curve of η_{bl} *vs.*ṡ. It is noticed that if $\chi \rightarrow 0.7$, η_{bl} becomes nearly constant at low ṡ. [See Figure. 5b.] This phenomanon is explained as follows. Generrally, $\sinh^{-1} Y \simeq Y$ if $Y \ll 1$. The term $(\sinh^{-1} Y)/Y$ in Eq. (26) approaches unity if $Y \equiv \beta_{2PM}^{\chi}\ \beta_{2PM}^{1-\chi}\, \dot{s} \ll 1$. The latter relation is satisfied only at $\chi > 0.7$ and $\dot{s} < 300\ \mathrm{sec}^{-1}$. Thus, the curve of η_{bl} *vs.* ṡ shows the tendency to be flat at low shear rate ($\dot{s} < 300\ \mathrm{sec}^{-1}$) if $\chi > 0.7$. [See Figure. 5b and Eq. (26).]

Rheological Phenomena Shown in Figure 1. From Figure 1, one notes that (i) η_{bl} decrease exponentially with χ approaching asymptotically to a constant valve of η_{bl} at a given ṡ, (ii) η_{bl} at a given χ is higher at smaller ṡ. These facts are explained from Eq. (26) as shown below.

(a) First we consider the fact described in item (ii). Generally

$$\sinh^{-1} Y = \ln\ [Y + (Y^2+1)^{1/2}]$$

where $Y = \beta_{2bl}\, \dot{s} = \beta_{2PM}^{1-\chi}\, \beta_{2PS}^{1-\chi}\, \dot{s}$. [See Eq. (26).] Thus, the function, $(\sinh^{-1} Y)/Y$, decreases with increasing ṡ since $\sinh^{-1} Y$ increase with ln ṡ wheresas the denominator Y increases directly in proportion to ṡ. By this reason, the curve of η_{bl} *vs.* χ locates higher at lower ṡ.

(b) Next, the fact described in item (i) will be considered. Both Newtonian and non-Newtonian terms in Eq. (26), includes the term $A\chi^2+B\chi+C$ which decreases with χ about exponentially reaching a minimum at $\chi \simeq 0.7$. See Figure 3. [Note: the existence of a minimum at $\chi=0.7$ can be shown by differentiating Eq. (15) with respect to χ, and by introducing the values of A(=a)=2.70·10^3 and B(=b)=−3.77·10^3. The Newtonian term also has a minium at $\chi \simeq 0.78$.] After reaching the minimum,the function $A\chi^2+B\chi+C$ increases gradually with χ. But the function of $\sinh^{-1} \beta_{2PM}^{\chi}\, \beta_{2PS}^{1-\chi}\, \dot{s}$ in Eq. (26) decreases with increasing χ. Thus, the two factors, $A\chi^2+B\chi+C$ and $\sinh^{-1} \beta_{2PM}^{\chi} \beta_{2PS}^{1-\chi}\, \dot{s}$, react in opposite ways keeping $\eta_2\ (bl)$ constant at $\chi > 0.7$. The Newtonian term $\eta_{\infty}(bl)$ in Eq. (26) includes the exponential factor exp (-0.4χ). Because of this factor, the increase in the factor $A\chi^2+B\chi+C$ with χ after passing the minimum is compensated keeping the $\eta_{\infty}(bl)$ term about constant. Because of the abovementioned behaviors of $\eta_{\infty}(bl)$ and $\eta_2(bl)$ terms, the curve of $\eta_{bl}\ [=\eta_{\infty}(bl)+\eta_2(bl)]$ *vs.* χ shows the features shown in Figure 1.

References

(1) T. Ree and H. Eyring, *J. Appl. Phys.*, **26**, 793, 800 (1955).
(2) A. F. Gabrysh, T. Ree, H. Eyring, N. Makee and I. Cutler, *Trans. Soc. Rheol.* **5**, 67(1961); K. Park and T. Ree

J. Korean Chem. Soc., **15**, 293 (1971).
(3) F. H. Ree, T. Ree and H. Eyring, *J. Eng. Mech. Div. Proc. Am. Soc. Civ. Engr.*, **EM1**, 41 (1960); C. H. Kim and T. Ree, *J. Korean Chem. Soc.*, **23**, 217.
(4) C. D. Han, *J. Appl. Polym. Sci.*, **18**, 481 (1974).
(5) C. D. Han and Y. W. Kim, *J. Appl. Polym. Sci.*, **19**, 2831 (1975).
(6) S. Krause, *J. Macromol. Sci. Revs. Macromol. Chem.*, **C7**, 251 (1972).
(7) H. Eyring, *J. Chem. Phys.*, **4**, 283 (1936).

The Linear Free Energy Relationship in Cinnamonitrile Derivatives

Sang Chul Shim[†] and Suk Kyoon Yoon

Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 131, Korea

(*Received August 19, 1981*)

Chemical shift differences of vinyl protons of *cis*- and *trans*-cinnamonitrile derivatives are very well correlated with (σ_I, σ_R^0), σ_P^+, and (F, R) $(r=0.9996\text{–}0.8946)$, much better correlation than the case of methyl cinnamates. *para*-Substituted and *trans*-cinnamonitrile derivatives have larger resonance contribution than *meta*-substituted and *cis*-derivatives.

Introduction

In our previous paper[1], we reported the linear free energy relationship (LFER) in methyl cinnamates studied by ^{1}H-NMR spectrometry. The chemical shift differences of α-vinyl protons of *trans*- and *cis*-methyl cinnamates are well correlated with Hammett substituent constant σ, $(\sigma_I, \sigma_R^0)^2$ and Swain and Lupton constant[3] $(F\& R)$ $(r=0.999\text{–}0.879)$. The resonance contribution is larger in *trans*- and *para*-substituted cinnamates than in *cis*- and *meta*-substituted cinnamates. One of the interesting observations is that the correlation is much better in *cis*-cinnamates than *trans*-cinnamates. It is suspected that the bulky alkoxycarbonyl group (-COOR) may have something to do with this phenomenon. For example, the bulky ester group will diminish the resonance effect substantially in *cis*-cinnamates by causing the nonplanarity of the compounds and the inductive effect will play the dominant role in *cis*-cinnamates as observed.

Therefore, we applied the same methodology to cinnamonitriles to test these kinds of effects. The linear and much smaller cyano group in cinnamonitrile compared to nonlinear, bulkier ester group in cinnamates will maintain the coplanarity even in *cis*-cinnamonitrile derivatives in contrast to cinnamates.

The chemical shift of α-vinyl protons of cinnamonitriles is measured and correlated with LFER parameters such as Hammett substituent constant (σ), Brown and Okamoto constant (σ_p^+), and Swain and Lupton constant $(F\ \&\ R)$. The same Hammett equation and its variations[4~6] used for cinnamates as shown below are applied.

$$\delta H_{\alpha,x} = \rho\sigma + \delta H_{\alpha,0} \qquad \text{(eq. 1)}$$

$$\delta H_{\alpha,x} = \rho_I\sigma_I + \rho_R\sigma_R + H_{\alpha,0} \qquad \text{(eq. 2)}$$

$$\delta H_{\alpha,x} = fF + rR + H_{\alpha,0} \qquad \text{(eq. 3)}$$

$$\lambda_p = (\rho_R/\rho_I)_p \qquad \text{(eq. 4)}$$

$$\lambda'_p = (r/f)_p \qquad \text{(eq. 5)}$$

$$\lambda_m = (\rho_R/\rho_I)_m \qquad \text{(eq. 6)}$$

$$\lambda'_m = (r/f)_m \qquad \text{(eq. 7)}$$

$$N_p = (\lambda_p)_{trans}/(\lambda_p)_{cis} \qquad \text{(eq. 8)}$$

$$N_p' = (\lambda_p')_{trans}/(\lambda_p')_{cis} \qquad \text{(eq. 9)}$$

$$N_m = (\lambda_m)_{trans}/(\lambda_m)_{cis} \qquad \text{(eq. 10)}$$

$$N_m' = (\lambda_m')_{trans}/(\lambda_m')_{cis} \qquad \text{(eq. 11)}$$

where F and R are the substituent constants corresponding to the field and resonance contribution proposed by Williamson and Norrington and f and r are their weighting factors. $\lambda_p(\lambda_p')$ and $\lambda_m(\lambda_m')$, so called the blending coefficients, represent the ratio of resonance and inductive (field) contribution of *para* and *meta* substituents and $N_p(N_p')$ and $N_m(N_m')$ represent the ratio of λ.

Experimental

Materials. Cinnamonitrile derivatives were synthesized from the corresponding cinnamic acids by the standard method[7,8] as described below. Thionyl chloride was added to cinnamic acid and the mixture was refluxed with stirring for 5–8 hours. Excess thionyl chloride was removed by evaporation and precooled ammonium hydroxide was added dropwise to the residue and stirred with magnetic bar for 5 hours at room temperature to get amide crystals. The amide was filtered with suction, washed with distilled water and dried in vacuo. The dry and finely powdered amide and thionyl chloride mixture was placed in a round bottomed flask and refluxed for 4–7 hours with stirring. The solvent was evaporated off and methylene chloride was added to the reaction mixture. The solution was washed with distilled water, aqueous sodium bicarbonate, and with distilled water.