

A Note on Intrinsic Viscosity-Temperature Relationships

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Intrinsic viscosities of polymethyl methacrylate solutions have been measured in acetone over the temperature range of 25–40°C. The samples were obtained by repeated careful fractionation from a 0.3% acetone solution with methanol as a precipitant. The molecular weights of the fractions used for this experiment were 1,288,000, 699,000, 544,000, and 185,000, as determined by osmometry. The viscometric measurements were carried out in an Ubbelohde viscometer and the kinetic energy correction was applied to the data. Measurements on each solution at the lowest temperature made both before and after the observations at higher temperatures were in good agreement. It was thus confirmed that the polymer chains were molecularly dispersed in the solutions. The intrinsic viscosities were calculated by the usual extrapolation to infinite dilution, making use of the least-squares method, and were sufficiently accurate to permit discussion of small changes with temperature.

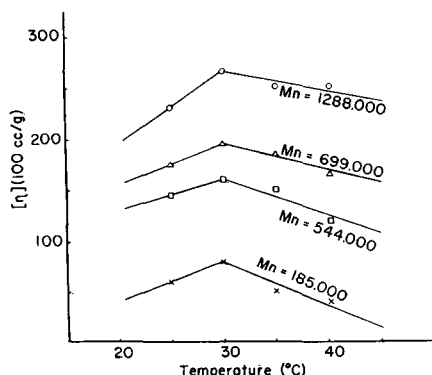


Fig. 1. The intrinsic viscosities of polymethyl methacrylate fractions in acetone plotted against temperature. The number-average molecular weight is indicated for each curve.

The plots of intrinsic viscosity vs. temperature are shown in Figure 1. It is seen that the intrinsic viscosity shows a maximum at about 30°C. for all the samples studied. Similar intrinsic viscosity-temperature behavior was also observed with polyethylenes from various sources in xylene.¹ It is of interest to clarify theoretically whether the observed maximum may be considered a general phenomenon.

The main purpose of this note lies in demonstrating that such behavior is in no way specific to these solutions but should be observed generally for polymer solutions, when their intrinsic viscosities are measured over a sufficiently wide range of temperatures. This phenomenon will be interpreted according to the theoretical treatment of intrinsic viscosities developed by Flory and Fox,² and the usefulness of the viscosity-temperature study will be suggested.

The results of the theory of Flory and Fox are summarized in the following equations:²

$$[\eta] = KM^{1/2}\alpha^3 \quad (1)$$

$$\alpha^5 - \alpha^3 = 2C_M M^{1/2} \varphi_1 (1 - \Theta/T) \quad (2)$$

$$K = \Phi(\bar{r}_0^2/M)^{3/2} \quad (3)$$

$$C_M = (27/2^{5/2}\pi^{3/2})(\bar{v}^2/NV_1)(\bar{r}_0^2/M)^{-3/2} \quad (4)$$

where $[\eta]$ is the intrinsic viscosity, M the molecular weight of the polymer, and α the linear expansion caused by "volume exclusion" interactions between remotely connected chain segments; φ_1 is a parameter representing the entropy contribution to the solvent-polymer interaction; Θ is the critical temperature for miscibility for a polymer homolog of infinite molecular weight in a given solvent; T is the absolute temperature, Φ is a constant which is the same for different polymer-solvent systems and \bar{r}_0^2 represents the unperturbed value of the mean-

square end-to-end length of the chain; \bar{v} is the partial specific volume of the polymer, V_1 the molar volume of the solvent, and N is Avogadro's number.

The effect of temperature on $[\eta]$ depends on the temperature coefficients of K and α . Usually K decreases slowly with increase in temperature owing to the increased thermal motion overcoming potential energy barriers to rotation about bonds of the chain molecule. The change in K with temperature for polyisobutylene and polystyrene,³ for example, amounts to only *ca.* -0.1 to -0.2% /°K. Thus we may conveniently write

$$K = J(1 - bT) \quad (5)$$

where J and b are constants characteristic of the particular polymer chain. This is equivalent to the just-mentioned experimental relation, and $K = K_{T=T_0} [1 - b'(T - T_0)]$ where T_0 is a certain standard temperature within the range covered by the experiment. We may regard b as $b'K_{T=T_0}/J$, and J as the value of K extrapolated to $T = 0^\circ\text{K}$. (It is not necessary that this extrapolated value be the true value at $T = 0^\circ\text{K}$.)

On the other hand, the effect of temperature on α results from the changes in (\bar{r}_0^2/M) and $\varphi_1(1 - \Theta/T)$ with temperature (cf. eqs. (2) and (4)). The temperature coefficient $\varphi_1(1 - \Theta/T)$ reflects the sign of the heat of dilution, being positive when the heat of dilution is positive. With the exception of some polar polymer-solvent combinations, a number of polymer-solvent pairs generally display positive heats of dilution. When this is the case, both of the factors $(\bar{r}_0^2/M)^{-1/2}$ and $\varphi_1(1 - \Theta/T)$ occurring in eq. (2) increase with temperature.

In order to formulate the above situation, we have obtained an approximate solution of eq. (2) for α :

$$\alpha \cong (20/27) + (c + A/9)^{1/2} \quad (6)$$

where $c = 0.02276$ and $A = 2C_M M^{1/2} \varphi_1(1 - \Theta/T)$. Equation (6) affords a satisfactory approximation, provided that the value of α does not exceed about 1.8, which has usually been the case for any polymer-solvent pair so far investigated. The dependence of α upon temperature is included only in A , which may be written from eqs. (3), (4), and (5):

$$A = A^*(1 - bT)^{-1}(1 - \Theta/T) \quad (7)$$

where $A^* = 2C_M M^{1/2} \varphi_1$. (The asterisk denotes the value extrapolated to $T = 0^\circ\text{K}$.)

The effect on the intrinsic viscosity of the re-

sulting increase in α^3 with temperature is directly modified, according to eq. (1), by the decrease in K with temperature. On substituting the expressions of eqs. (5) and (6) for K and α into eq. (1), we obtain:

$$[\eta] = J(1 - bT)M^{1/2}[(20/27) + (c + A/9)^{1/2}]^3 \quad (8)$$

According to eqs. (7) and (8) the condition for $d[\eta]/dT = 0$ becomes:

$$(A^*/9)(1 - bT_m)^{-1}(1 - \Theta/T_m) = (27/20)[(A^*/9)(\Theta/bT_m^2) - c]^{1/2} - c \quad (9)$$

which gives the temperature T_m at which the $[\eta]$ vs. T curve shows a maximum. When c is negligible compared with the other terms (as is usually the case), eq. (9) may be transformed to an approximate simple relationship:

$$(1 - \Theta/T_m)^{3/2}/(\Theta/T_m) = (27/20)(A^*/9)^{1/2}(1 - bT_m)^{3/2}/bT_m \quad (10)$$

Equation (10) indicates that T_m is lower for lower Θ points (better solvents) and is higher for smaller values of b (more flexible polymer chains) and for larger values of A^* (higher molecular weights).

To provide a quantitative examination of the above theoretical results, the effects of the molecular weight of the polymer, the chain flexibility, and the type of solvent upon the intrinsic viscosity-temperature behavior will be discussed. Unfortunately, there have been very few experimental studies in which values for all three constants, b , Θ , and $C_M \varphi_1$, have been obtained. The results of Fox and Flory on intrinsic viscosities of polystyrene in various solvents³ are probably the most reliable data available for the present purpose. Making use of the values determined by them for the constants in eq. (9), we have calculated T_m for various molecular weights of polystyrene in toluene; the results are given in Table I.

TABLE I
 T_m Calculated as a Function of Molecular Weight of Polystyrene in Toluene
($b = 0.00125$, $C_M \varphi_1 = 0.30 \times 10^{-2}$ (25°C.), $\Theta = 160^\circ\text{K}$.)

$M \times 10^{-3}$	$A^*/9$	$T_m, ^\circ\text{K}$.	$T_m, ^\circ\text{C}$.
6.4	0.0530	278	5
57.6	0.1591	302	29
160	0.2651	325	52
314	0.3711	345	72
640	0.5302	360	87

The value of T_m thus estimated varies considerably with the molecular weight of the polymer. It is seen, however, that T_m lies in the range 30–52°C. for the samples having molecular weights in the range 60,000–160,000. This seems to be consistent with the experimental results: Table VI of reference 3 shows that T_m exists within the ranges 25–55°C. and 25–35°C. for the 144,000 and 456,000 molecular weight fractions, respectively. In this case, however, $[\eta]$ did not show as distinct a maximum as has been observed in our experiment, owing primarily to the weaker dependence of α and K on temperature for the nonpolar polystyrene-toluene system than for the polar polymethyl methacrylate-acetone system.

Furthermore, the question might arise as to why, in our case, T_m is nearly independent of the molecular weight of the polymer, as was shown in Figure 1. Indeed, the above treatment indicates that in general, T_m depends upon the molecular weight of the polymer, but this does not mean that the treatment has failed to explain our result, as we shall show. No detailed viscometric studies of polymethyl methacrylate solutions in acetone, from which b , Θ , and A^* could be evaluated, have yet been published; if the above treatment is applicable, however, our experimental result can be utilized to estimate these constants in the following way.

It is easily seen from eq. (10) that the condition under which T_m is approximately independent of the molecular weight of the polymer is as follows:

$$A^*/9 \cong 1$$

For Θ we obtain a value of 147°K. from the data of Schulz and Doll⁴ on thermodynamic properties of this system, by making use of the relation² $\Theta = \kappa_1/\varphi_1$. Employing these values for A^* and Θ and 303°K. for T_m , we computed b by eq. (10) as 0.00177. In view of the magnitudes of b so far obtained for polystyrene, polyisobutylene, and other polymers,⁵ this value of b for polymethyl methacrylate seems consistent with the information on its molecular flexibility.⁶ Recalculation with this value of b in eq. (9) gives $T_m = 303^\circ\text{K.}$ for $A^*/9 = 0.78$. (This value of A^* , and $C_M^*\varphi_1$ assumed conveniently as 0.9×10^{-2} , corresponds to $M = 152,000$.) For $A^*/9 = 1.99$, $T_m = 308.5^\circ\text{K.}$ (and with the previous assumption, $M = 1,000,000$). It must be noted that even in this case, T_m is not entirely independent of the molecular weight of the polymer, but its variation with the molecular weight is comparatively small.

The preceding experimental evidence and theoretical treatment lead to the expectation that for polymer solutions in general, intrinsic viscosities should show maxima if they are measured as a function of temperature at sufficiently small intervals and over a sufficiently wide range. If this is true, T_m is important because it is a characteristic temperature of a given polymer-solvent combination, just as is the Θ -temperature. Polymer molecules take the most expanded configuration at this temperature, whereas they take the most compact configuration at the Θ -temperature. The dependency of $[\eta]$ on the molecular weight of the polymer would therefore be greatest at T_m , suggesting that T_m is the most suitable temperature for viscometric molecular weight determination, so long as no experimental difficulty arises at this temperature.

Although the Θ temperature depends upon only the thermodynamic properties of the solution (a long-range effect), T_m is affected by the chain flexibility (a short-range effect) as well. The measurement of T_m thus provides a method for determination of the constant b , which gives a measure of the chain flexibility (or, strictly speaking, of the potential energy of rotation about bonds of the chain molecule). Here, a convenient method for finding b will be proposed. In the special case when $(27/20)(A^*/9)^{1/4} = 1$ (that is, $A^* = 3.658$), eq. (10) becomes:

$$T_m^2 = \Theta/b \quad (11)$$

Therefore, suitable choice of a molecular weight of the polymer (for the known value of $C_M\varphi_1$) and of a solvent (i.e., the value of Θ) enables us to estimate b by eq. (11) from the measurement of T_m .

Equation (11) can also be utilized to determine the sign of the temperature coefficient of $[\eta]$ of a given polymer solution. In Table II the values of T_m are calculated by use of eq. (11) for a few polymers having molecular weights which fulfill the condition $(27/20)(A^*/9)^{1/4} = 1$ in various solvents. The values cited for b , Θ , and $C_M\varphi_1$ are again from the data of Fox and Flory.³ The values of T_m thus calculated represent well the sign of the observed temperature coefficient of $[\eta]$: for molecular weights higher than those given in Table II, column 6, the temperature coefficient of $[\eta]$ is positive when the measuring temperatures are below T_m , and conversely. This is shown in the last column in Table II, the figures in this column denoting the temperature and molecular weight ranges in which intrinsic viscosities were measured.

TABLE II
 T_m Calculated by Use of Eq. (11) for Various Polymer-Solvent Systems for a Particular Molecular Weight

System		b	Θ , °K.	$C_M\varphi_1$ $\times 10^2$	$M \times 10^{-4}$	T_m , °K.	$d[\eta]/dT$ (measured)
Polymer	Solvent						
Polystyrene	Benzene	0.00125	100	0.29 ^a	102	283	Negative, 303–328°K. ($M \times 10^{-4} = 127$)
	Cyclohexane	0.00125	307	0.35 ^a	69	496	Positive, 307–328°K. ($M \times 10^{-4} = 9.2$ – 127)
	Dichloroethane	0.00125	190	0.23 ^a	160	390	Positive, 295–340°K. ($M \times 10^{-4} = 162$)
Polyisobutylene	Benzene	0.00109	297	0.55 ^b	89.5	523	Positive, 293–338°K. ($M \times 10^{-4} = 18$ – 188)
	Cyclohexane	0.00109	126	0.42 ^b	153.2	340	Nearly zero, 293–333°K. ($M \times 10^{-4} = 146$)
	Toluene	0.00109	261	0.43 ^b	146.3	489	Positive, 273–358°K. ($M \times 10^{-4} = 146$)
	Ethylbenzene	0.00109	250	0.37 ^b	197.6	480	Positive, 273–348°K. ($M \times 10^{-4} = 188$)
	Diisobutylene	0.00109	84	0.12 ^b	1879	82.5	Negative, 293–358°K. ($M \times 10^{-4} = 188$)
	<i>n</i> -Hexadecane	0.00109	175	0.11 ^b	2236	401	Nearly zero at 323°K. ($M \times 10^{-4} = 146$)

^a At 25°C.

^b At 0°C.

Furthermore, the above treatment could be profitably applied to the determination of molecular weights of polymers. When T_m , Θ , and b are known, we can evaluate the values for A^* by eq. (9). Since $A^* = 2C_M^*\varphi_1M^{1/2}$, the relative magnitudes of the molecular weights are easily obtained from the measurement of T_m for a series of polymer homologs. Moreover, when $C_M^*\varphi_1$ or the molecular weight of a sample is known, the molecular weights of the polymer homologs can be determined from the intrinsic viscosity-temperature studies.

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Synopsis

In the course of studying the intrinsic viscosity-temperature relationship for polymethyl methacrylate in acetone, it was found that the intrinsic viscosities $[\eta]$ of four samples of different molecular weights showed a maximum at about 30°C. This phenomenon can be interpreted according to the Flory-Fox theory of intrinsic viscosities. An equation has been derived from their results that gives the condition for the existence of the temperature T_m at which the $[\eta]$ vs. temperature curve shows a maximum. This equation indicates that T_m is lower for lower Θ points (better solvents) and higher for more flexible chains and for higher molecular weights. It may thus be concluded that such behavior as was found here is in no way specific to polymethyl methacrylate in acetone but should be observed generally for polymer solutions when their intrinsic viscosities are measured over sufficiently wide ranges of temperature. T_m is important because it is a characteristic temperature of a given polymer-solvent combination, just as is the Θ temperature. Polymer molecules take the most expanded configurations at this temperature, whereas they take the most compact configurations at the Θ temperature. Although the Θ temperature depends upon only the thermodynamic properties of the solution, T_m is also affected by the chain flexibility. The measurement of T_m thus provides a method for estimating a parameter expressing the chain flexibility. The resulting equations can also be utilized to determine the sign of the temperature coefficient of $[\eta]$ of a given polymer solution in a given temperature range.

Résumé

En étudiant la relation entre la viscosité intrinsèque et la température pour le polyméthacrylate de méthyle dans l'acétone, on a trouvé que la viscosité intrinsèque $[\eta]$ présente un maximum aux environs de 30°C pour des échantillons de poids moléculaires différents. Ce phénomène peut être interprété au moyen de la théorie de Flory et Fox concernant la viscosité intrinsèque. A partir de leurs résultats on a tiré une équation qui donne la condition d'existence de la température T_m vers laquelle la courbe $[\eta]$ en fonction de la température présente un maximum. Cette équation indique que T_m est plus bas pour des points Θ plus bas (meilleurs solvants) et est plus haut pour des chaînes plus flexibles et pour des poids moléculaires plus hauts. On peut donc conclure qu'un tel comportement n'est pas spécifique au polyméthacrylate de méthyle dans l'acétone, mais pourrait être généralement observé pour des solutions de polymère, pour autant que leurs viscosités, intrinsèques soient mesurées sur des domaines suffisamment larges de température. T_m est important parce que c'est une température caractéristique pour une combinaison polymère-solvant donnée, de même que la température Θ . Les molécules de polymère prennent la configuration la plus étendue à la température T_m , tandis qu'elles prennent les configurations les plus compactes à la température Θ . Alors que la température Θ dépend seulement des propriétés thermodynamiques de la solution, T_m est aussi affecté par la flexibilité de la chaîne. La mesure de T_m fournit donc une méthode pour l'estimation d'un paramètre qui exprimerait la flexibilité de la chaîne. Les équations qui en résultent peuvent aussi être utilisées pour déterminer le signe du coefficient de température de $[\eta]$ pour une solution de polymère donnée dans un domaine de température donné.

Zusammenfassung

Im Verlaufe von Untersuchungen über die Temperaturabhängigkeit der Viskositätszahl von Polymethylmethacrylaten in Aceton wurde gefunden, dass die Viskositätszahl $[\eta]$ bei Proben mit verschiedenem Molekulargewicht bei etwa 30°C ein Maximum aufweist. Diese Erscheinung kann durch die Theorie der Viskositätszahl von Flory und Fox erklärt werden. Aus den Ergebnissen der genannten Theorie wurde eine Beziehung abgeleitet, die die Bedingungen für das Auftreten einer Temperatur, T_m , angibt bei der die $[\eta]$ -Temperatur-Kurve ein Maximum aufweist. Diese Beziehung zeigt, dass T_m für niedrigere Θ -Punkte (bessere Lösungsmittel) tiefer liegt und bei biegsameren Ketten und höheren Molekulargewichten höhere Werte erreicht. Es kann daraus geschlossen werden, dass ein Verhalten, wie es hier gefunden wurde, in keiner Weise für Polymethylmethacrylat in Aceton spezifisch ist, sondern allgemein an Polymerlösungen beobachtet werden sollte, sofern nur ihre Viskositätszahlen über einen genügend grossen Temperaturbereich gemessen werden. T_m ist deshalb wichtig, weil diese Temperatur genau so wie die Θ -Temperatur, eine für ein bestimmtes Polymer-Lösungsmittelpaar charakteristische Temperatur ist. Die Polymermoleküle nehmen bei der T_m -Temperatur die am meisten gestreckte Konfiguration ein, während sie bei der Θ -Temperatur in der kompaktesten Konfiguration vorliegen. Im Gegensatz zur Θ -Temperatur, die nur von den thermodynamischen Eigenschaften der Lösung abhängt, wird T_m auch von der Biegsamkeit der Ketten beeinflusst. Die erhaltenen Gleichungen können auch zur Bestimmung des Vorzeichens des Temperaturkoeffizienten von $[\eta]$ einer bestimmten Polymerlösung in einem bestimmten Temperaturbereich verwendet werden.

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