Intrinsic Viscosity of Polymer Solutions at High Shear Rates

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Synopsis

Although low-shear intrinsic viscosity is a well-accepted tool for polymer characterization, it often happens (particularly with increasing molecular weights) that it is easier to detect the high-shear (second) Newtonian viscosity η_2 rather than its low shear counterpart. It has also been predicted that because of a higher degree of order, due to disentanglement and orientation, high-shear viscosity data should simplify the prevailing correlations. The possibility of using high-shear viscometric data for polymer characterization was examined by determining intrinsic viscosities for several polyisobutylene samples through extrapolation of the high-shear ultimate viscosity numbers, UVN, to zero concentration: $[\eta]_2 = \lim \mathrm{UVN}_{C\to 0} = \lim_{C\to 0} (\eta_2 - \eta_s)/\eta_s C$, where η_s is the viscosity of the pure solvent. Five samples of unfractionated polyisobutylene (molecular weights of 1.1×10^6–6.6×10^6) in toluene, kerosene, decalin, and gas oil at concentrations of 0.05–2.4 g./dl. were studied. Higher dilution was avoided because of the problem of onset of turbulence. The absence of shear degradation was ascertained by measuring low-shear intrinsic viscosity data before and after the polymer was exposed to high-shear conditions. The data show two types of behavior: for the lower molecular weight samples in the low-viscosity solvents the UVN decreases linearly with dilution, and for the higher molecular weights and higher solvent viscosities the UVN increases with high dilution, i.e., shows an upturn effect. The first type of data can be successfully correlated with appropriate molecular weights by using a typical Mark-Houwink equation. The exponents in these relationships are in the range of 0.28–0.64, increasing systematically with decrease of solvent viscosity and independent of the "goodness" of the latter. The data that show an upturn effect are not currently amenable to reliable extrapolation techniques. The upturn, however, predicts the conformation of very flexible, isolated polymer chains in viscous solvents under conditions of high shear.

Introduction

Intrinsic viscosity determination has become a basic tool for polymer characterization. Most work has, however, been confined to low-shear conditions. This study utilizes high-shear data, the domain of the ultimate, or second Newtonian viscosity, η_2, by extrapolating the "ultimate viscosity numbers," UVN, to zero concentration:

$$[\eta]_2 = \lim \mathrm{UVN}_{C\to 0} = \lim_{C\to 0}(\eta_2 - \eta_s)/\eta_s C \qquad (1)$$

where η_s is the viscosity of the pure solvent.

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The reasons for going to high-shear conditions are two: the first Newtonian viscosity is frequently unobtainable for relatively high molecular weight polymers, and the range of the second Newtonian viscosity is believed to entail a higher degree of order, i.e., disentangled and oriented chains.

The difficulties encountered in high-shear viscometry still eliminate extensive use of this challenging domain. The major hindrances are polymer shear degradation and interference of turbulence.

An attempt at relating UVN data to molecular weights of various polymers has been previously discussed.[1-5] However, those empirical correlations are based on values of UVN at finite concentrations, which showed a plateau effect (independent of concentration). Other workers[6-8] who studied high-shear viscometry of extremely dilute solutions were able to obtain the extrapolated intrinsic viscosities $[\eta]_2$, but no effort at direct correlation with molecular weights was made.

The flexibility and deformation of a polymer chain under high-shear conditions have a marked effect upon its final dimensions, which apparently shows up in the dependence of UVN on concentration.

Experimental

Five samples of commercial polyisobutylene (unfractionated) were tested for the first and second intrinsic viscosities in four different solvents. The range of molecular weights $(\bar{M}_v)$ is 1.1×10^6 to 6.6×10^6.

The polymer samples were generously provided by the Enjay Company, Linden, New Jersey, and B.A.S.F. AG, Ludwigshafen Am Rhein. Details are listed in Table I.

TABLE I
Commercial Polyisobutylenes

Designation, polyisobutylene	Supplier	$\bar{M}_v \times 10^6$
L-100	Enjay	1.1
L-120	Enjay	1.64
L-140	Enjay	2.04
B-200	B.A.S.F.	5.6
L-250	Enjay	6.6

The molecular weights were calculated from low-shear intrinsic viscosity data in cyclohexane at 30°C. according to the following equation:[9]

$$[\eta]_1 = 2.65 \times 10^{-4}\bar{M}_v^{0.69} \tag{2}$$

The solvents used are listed in Table II together with the proper viscosities at the testing temperatures.

Dilute solutions were carefully prepared with gentle mixing in order to prevent shear degradation. The range of concentration for both low-shear and high-shear studies differed for each polymer–solvent pair. While at low-shear the concentrations were extremely low, making linear extrapolations of viscosity numbers possible, the concentration level for high-shear

TABLE II
Solvents for Intrinsic Viscosity Tests

Solvent	Temp., °C.	Viscosity, cp.
Toluene (reagent)	30	0.54
Kerosene (technical)	30	1.175
Decalin (technical)	30	1.94
Gas oil (technical)	45	3.05

studies was necessarily higher. The lower boundary of concentration for high-shear work is dictated by the onset of turbulence, while the upper one is simply controlled by the possibility of detecting the second Newtonian viscosity. The extreme concentrations for $[\eta]_2$ were 0.05 and 2.4 g. per 100 cm.^{3}, properly.

The instrumentation for low-shear data consisted of conventional capillary viscometers (the Ubbelohde) and a multispeed rotational viscometer, the Epprecht Rheomat 15, manufactured by Contraves A. G., Zurich. The latter makes feasible the accurate measurement of viscosity at fifteen fixed speeds, providing shear rates from 11 to 1786 sec.$^{-1}$. The successful use of this rotational viscometer for low-shear intrinsic viscosities has been published elsewhere.[10] The high-shear viscometer consists of stainless-steel capillaries operated under pressure of nitrogen gas; this instrument is described elsewhere.[11] After a study of the end-effect corrections large ratios of capillary length to radius were used. Details are given in Table III.

TABLE III
Geometry of Capillaries in the High-Shear Viscometer

Number	Symbol used in figures	Radius R, cm.	Length L, cm.	Ratio L/R
1	O	0.0436	24.8	570
2	△	0.0436	34.8	798
3	□	0.0436	44.9	1030

The temperature was carefully controlled to within ±0.1°C. The rates of shear at the wall were calculated from flow rate data after kinetic energy and Rabinowitsch[12] corrections had been applied. The largest shear stresses and shear rates were 5×10^4 dyne/cm.^{2} and 4×10^5 sec.$^{-1}$, respectively. Each solution was checked before and after high-shear tests for possible shear degradation by means of low-shear viscosity measurements. Whenever evidence of degradation was found, the data were rejected.

Results

The major effort was directed toward obtaining accurate second-Newtonian viscosity data from the flow curves for each polymer sample for various solvents and concentrations. To extrapolate to zero concentration and so obtain the intrinsic viscosity, care was taken to get η_2 for solutions
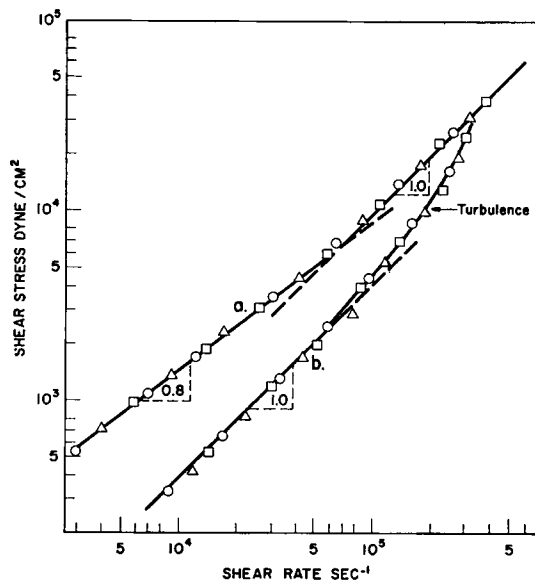
Fig. 1. Flow curves of PIB solutions in decalin at 30°C.:   (a) L-100, C = 1.19 g./dl.;
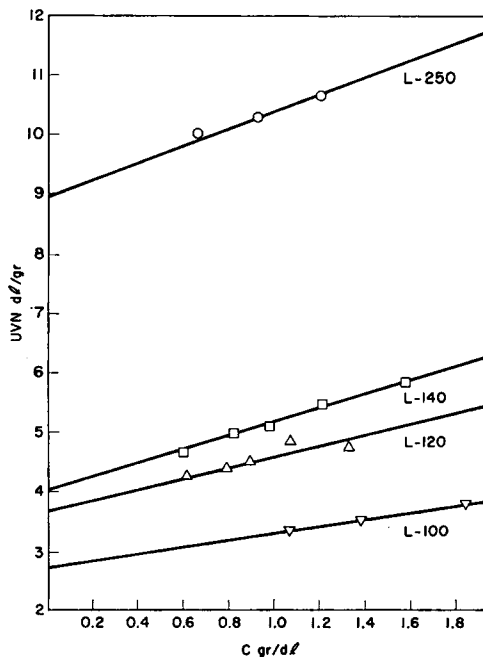(b) L-150, C = 0.165 g./dl.

Fig. 2. Ultimate viscosity number versus concentration for PBI in toluene at 30°C.
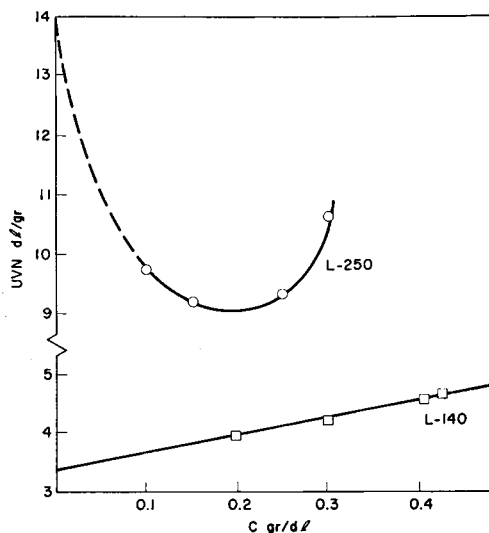
Fig. 3. Ultimate viscosity number versus concentration for PIB in kerosene at 30°C.
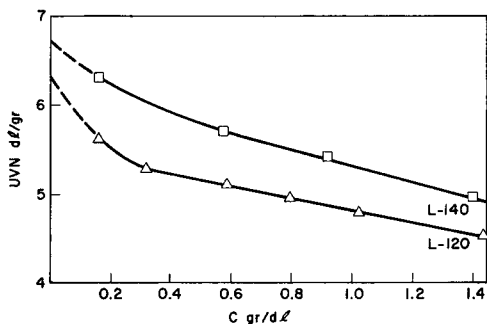

Fig. 4. Ultimate viscosity number versus concentration for PBI in decalin at 30°C.

as dilute as possible. The choice of highly viscous solvents aided this approach.

Typical high-shear rate flow curves are shown in Figure 1. The ultimate viscosity numbers UVN, defined in eq. (1), were calculated and plotted against concentration for each polymer–solvent pair. Typical results are shown in Figures 2–5.

The extrapolated values of UVN are summarized as $[\eta]_2$ in Table IV and compared with the appropriate low-shear intrinsic viscosities $[\eta]_1$.

All polymers in toluene (the least viscous solvent) were characterized by a linear increase of UVN with increase of concentration over the entire range (Fig. 2). With more viscous solvents and lower concentrations the shape of the curves changes, exhibiting negative slopes, particularily in the
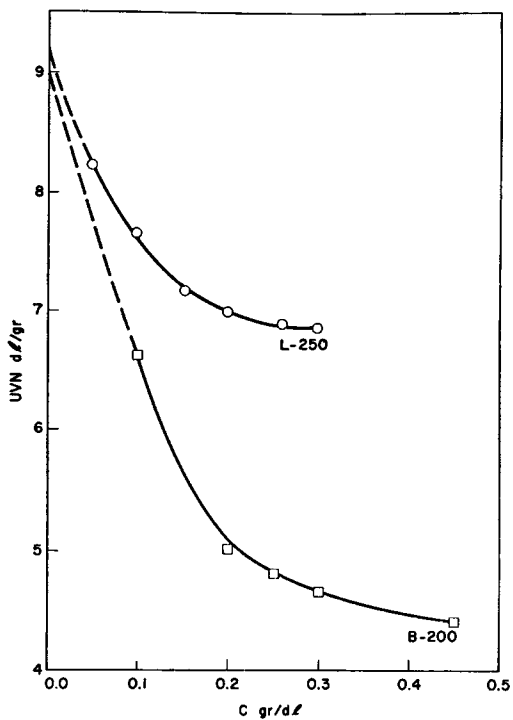
Fig. 5. Ultimate viscosity number versus concentration for PIB in gas oil at 45°C.
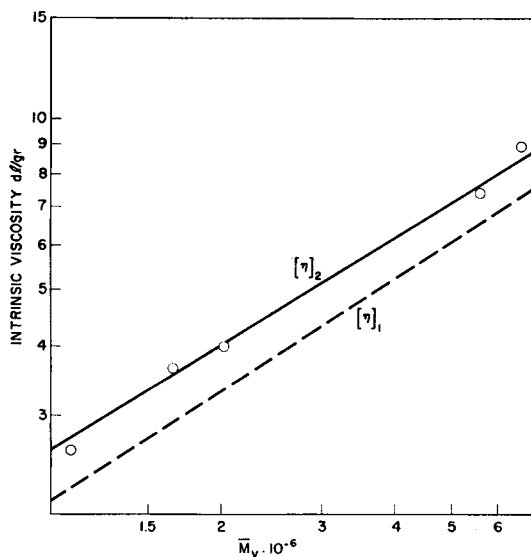

Fig. 6. Intrinsic viscosity versus molecular weight for PIB in toluene at 30°C.: (——)
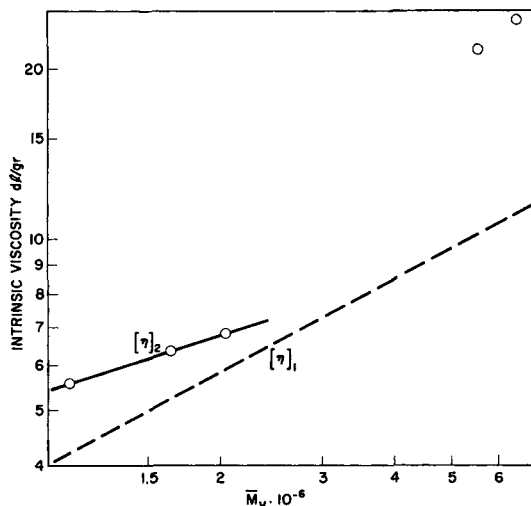high shear; (- - -) low shear.

Fig. 7. Intrinsic viscosity versus molecular weight for PIB in decalin at 30°C.:   (——)
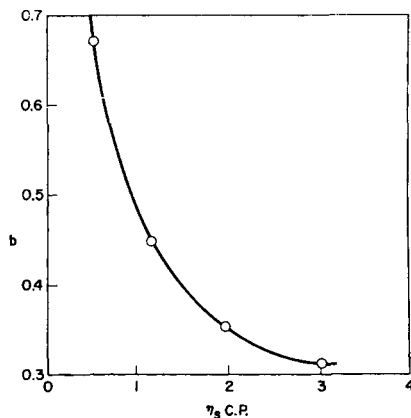high shear; (- - -) low shear.

Fig. 8. Exponent b versus viscosity η_s of solvent.

case of the higher molecular weight samples.   This upturn effect of UVN
upon dilution is most clearly described in Figure 5, which represents the
extreme condition of highest molecular weight and most viscous solvent.
In these cases reliable extrapolations are obviously prevented.

The values of $[\eta]_2$ of all polyisobutylene (PIB) samples in toluene and
of those associated with the three lower molecular weight samples (L-100,
L-120 and L-140) in all other solvents were correlated with the appropriate
molecular weights by using a typical Mark-Houwink equation:

$$[\eta]_2 = K' \bar{M}_v^{\,b} \tag{3}$$

TABLE IV
Intrinsic Viscosities at Low-Shear and High-Shear
Rates for Polyisobutylene

PIB and $\bar{M}_v$ ($\times 10^6$)	Solvent	$[\eta]_1$, dl./g.	$[\eta]_2$, dl./g.	Temp., °C.	Concn. for high shear, g./dl.
L-100, 1.1	Toluene	2.23	2.75	30	1.1 –2.4
	Kerosene	2.55	2.65	30	0.2 –0.8
	Decalin	4.3	5.6	30	0.15–1.4
	Gas oil	2.35	2.9	45	0.1 –0.6
L-120, 1.64	Toluene	2.9	3.68	30	0.6– 1.4
	Kerosene	3.65	3.3	30	0.2 –0.8
	Decalin	5.25	6.3	30	0.1 –1.5
	Gas oil	2.95	3.35	45	0.1 –0.4
L-140, 2.0	Toluene	3.4	4.0	30	0.6 –1.6
	Kerosene	3.95	3.4	30	0.2 –0.5
	Decalin	5.95	6.7	30	0.1 –1.6
	Gas oil	3.35	3.62	45	0.1 –0.4
B-200, 5.6	Toluene	6.6	7.3	30	0.7 –1.6
	Kerosene	8.3	13	30	0.1 –0.4
	Decalin	10.5	21.5	30	0.05–0.5
	Gas oil	6.0	9	45	0.1 –0.5
L-250, 6.6	Toluene	7.4	9	30	0.6 –1.2
	Kerosene	9.3	14	30	0.1 –0.3
	Decalin	11.0	24	30	0.05–0.6
	Gas oil	6.7	9.2	45	0.05–0.3

These correlations are shown on log–log plots, Figures 6 and 7. The exponents b vary in the range of 0.28–0.64, increasing continuously with decrease of solvent viscosity without any systematic dependence of the "goodness" of the solvent. The effect of solvent viscosity is shown in Figure 8.

The numerical values of K' and b are shown in Table V.

TABLE V
Constants of Eq. (3)

Solvent	Temp., °C.	K'	b
Toluene	30	9×10^{-4}	0.64
Kerosene	30	8.5×10^{-3}	0.42
Decalin	30	6.4×10^{-2}	0.32
Gas oil	45	6.0×10^{-2}	0.28

Discussion

It is shown in Table IV that as a rule $[\eta]_2 > [\eta]_1$ even without the upturn effect. The polymer solutions, however, were definitely shear-thinning until the second Newtonian range was reached, indicating that $[\eta]_2$ should be less than $[\eta]_1$. The discrepancy lies in the different concentration levels of low-shear and high-shear studies. By measuring with the
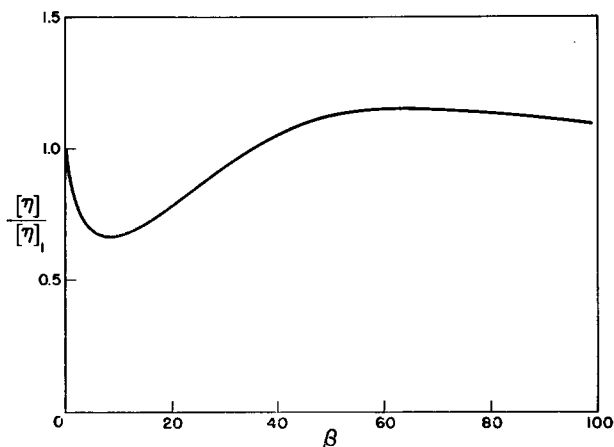
Fig. 9. Change of intrinsic viscosity with shear for complete flexible chains (Peterlin[13]).

rotational viscometer the low-shear viscosities of the same samples that were studied under high-shear and by extrapolating to zero concentration a modified low-shear intrinsic viscosity $[\eta]_1^*$ was obtained, which was definitely higher than either $[\eta]_2$ or $[\eta]_1$. This clearly shows that exact extraploations to zero concentration necessitate work with extremely dilute solutions.

The range of the exponents b in eq. (3), 0.28–0.64, which is lower than normally found in low-shear viscometry, resembles other correlated data.[3,4] This points out that the second intrinsic viscosity has a weaker dependence on molecular weight. It also agrees with the fact that the ratio $[\eta]_0/[\eta]_\infty$ increases with increase of molecular weight.[13] By relating Golub's data[6] to the appropriate molecular weights an exponent of 0.44 is obtained, whereas the high-shear data of Phillippoff and Hess[14] for nitrocellulose solutions correlate with $M_v^{0.14}$. In those rigid polymers the conformation of the chains at high-shear conditions approaches that of fully oriented long rods. In the extreme case the dependence of intrinsic viscosity on molecular weight will diminish.[15] The effect of solvent viscosity on the exponent b, described in Figure 8, points out that the chains are eventually more stretched when sheared in more viscous solvents.

The dramatic uprise of UVN with dilution, clearly verified when extremely high molecular weights and more viscous solvents were incorporated, indicates the response of flexible, isolated chains to high-shear stress. In these conditions the deformation of the chains induces expansion as crowding gradually diminishes. Such behavior is predicted and analyzed by Peterlin and his associates in various publications.[13,16−18] The controlling factor that determines the shear dependence of intrinsic viscosity, according to Peterlin, is β, defined as

$$\beta = M[\eta]_1 \eta_s G/RT \tag{4}$$

where G = shear rate, T = temperature, and M = molecular weight. Whereas in rigid polymer $[\eta]$ decreases monotonically with β, flexible chains show an uprise of $[\eta]$ at increasing values of β. Typical behavior is described in Figure 9. Experimental evidence[13,16-18] verified the prediction that the proper conditions for the exhibition of chain expansion due to increasing flexibility are high shear, long chains of soft polymers, very viscous solvents, and high dilutions. Our data agree qualitatively with this approach, in which the expansion of flexible chains overpasses the effects of hydrodynamic interaction and chain orientation.

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Résumé

Alors que la viscosité intrinsèque à faible cisaillement est un outil généralement accepté pour caractérisér les polymères, il est arrive souvent (particulièrement avec des poids moléculaires croissants) qu'il est plus facile de détecter la viscosité Newtoniene à cisaillement éleve η_2 plutôt que sa contrepartie à faible cisaillement. On a également pu prédire que sur la base d'un degré d'ordre plus élevé, dû à l'orientation et au désengagement, les résultats de viscosité à cisaillement élevé simplifieraient les corrélations existantes. La posilité d'utiliser des données viscosimétriques à cisaillement élevé pour caractériser les polymères a été examinée en déterminant les viscosités intrinsèques pour de nombreux échantillons de polyisobutylène par extrapolation de leur indice viscosimétrique limite à tensions élevées, UVN, à concentration nulle: $[\eta]_2 = \lim_{C \to 0} = \lim_{C \to 0} \eta_2 - \eta_3/\eta_3 C$; η_2 = viscosité du solvant pur. Cinq échantillons de polyisobutylène (non-fractionné (domaine de poids moléculaires de 1.1×10^6–6.6×10^6) ont été étudiés dans le toluène, le kérosène, la décaline et l'huile à des concentrations variant de 0.05 à 2.4 g/dl. Une dilution plus élevée à été évitée à cause du problème de la turbulence. L'absence de dégradation par cisaillement a été assurée en mesurant la viscosité intrinsèque à faible cisaillement avant et après que le polymère eut été exposé à des conditions de cisaillement

élevées. Les résultats montrent deux types de comportement. Pour les échantillons de poids moléculaires plus faibles dans des solvants de faible viscosité, UVN décroît linéairement avec la dilution. Toutefois, pour les poids moléculaires plus élevés et les viscosités de solvant plus élevées, UVN croît avec une dilution croissante, c'est-à-dire, montre un effet contraire. Le premier type de résultat peut être corrélié avec succès, avec succès, avec les poids moléculaires appropriés en utilisant l'équation typique de Mark-Houwink. Les exposants dans cette relation sont de l'ordre de 0.28 à 0.64, croissant de façon systématique avec la diminution de viscosité du solvant et indépendamment de la qualité bonne ou mauvaise de ces derniers. Les résultats qui montrent un effet renversé ne sont pas valables de façon habituelles par des techniques d'extrapolation. Leur renversement du diagramme toutefois, prédit une conformation de chaîne polymérique isolée très flexible dans des solvants visqueux dans des conditions de cisaillement élevé.

Zusammenfassung

Während die bei niedriger Schubspannung ermittelte Viskositätszahl eine zur Charakterisierung von Polymeren anerkannte Grösse darstellt, ist es oft (besonders bei zunehmenden Molekulargewichten) leichter, die (zweite) Newton'sche Viskositätszahl η_2 bei hoher Schubspannung zu bestimmen als ihr Gegenstück bei niedriger Schubspannung. Es wurde auch vorausgesagt, dass die bei hoher Schubspannung ermittelten Viskositätsdaten wegen des höheren Ordnungsgrades—eine Folge der Entwirrung und Orientierung —die vorherrschenden Zusammenhänge vereinfachen sollten. Die Möglichkeit, Viskositätsdaten aus Messungen bei hoher Schubspannung zur Charakterisierung von Polymeren zu verwenden, wurde an Hand einer Bestimmung der Viskositätszahlen für mehrer Polyisobutylen-Proben durch Extrapolation der äussersten bei hoher Schubspannung ermittelten Viskositätszahl (UVN) auf die Konzentration null untersucht: $[\eta]_2 = \lim \text{UVN}_{c \to 0} = \lim_{c \to 0} \eta_2 - \eta_2/\eta_s C$. η_s = Viskosität des reinen Lösungsmittels. Fünf Proben von nichtfraktioniertem Polyisobutylen (Molgew.-Bereich von $1,1 \cdot 10^7$ bis $6,6 \cdot 10^6$) wurden in Toluol, Kerosin, Dekalin und Gasöl im Konzentrationsbereich von 0,05–2,4 g/dl untersucht. Wegen der Möglichkeit eines Auftretens von Turbulenz wurde eine grössere Verdünnung vermieden. Sichergestellt wurde das Fehlen eines Abbaus bei Scherung durch Messung der Viskositätszahl bei niedriger Scherspannung, bevor und nachdem das Polymere der hohen Schubspannung ausgesetzt wurde. Die Daten zeigen zwei verschieden Verhaltensweisen. Bei den Proben mit niedrigerem Molgewicht nimmt in Lösungsmitteln mit niedriger Viskosität UVN linear mit der Verdünnung ab; dagegen nimmt bei höheren Molgewichten und Lösungsmitteln mit höherer Viskosität UVN mit höherer Verdünnung zu, d.h. sie zeigt einen Aufwärtswendungseffekt. Den ersten Datentypus kann man unter Verwendung einer typischen Mark-Houwink-Gleichung erfolgreich mit den entsprechenden Molekulargewichten korrelieren. Die Exponenten in diesen Beziehungen liegen im Bereich von 0,28–0,64; sie nehmen systematisch mit abnehmender Viskosität des Lösungsmittels und unabhängig von dessen "Güte" zu. Die Daten, die einen Aufwärtswendungseffekt zeigen, können nicht in üblicher Weise verlässlich extrapoliert werden. Die Aufwärtswendung spricht aber für eine Konformation sehr flexibler isolierter Polymerketten in viskosen Lösungsmitteln bei hoher Schubspannung.