

# Flow Relationships at High Shear in Concentrated Polyisobutene Solutions\*

ROGER S. PORTER and JULIAN F. JOHNSON

*California Research Corporation, Richmond, California*

## I. INTRODUCTION

Several investigators have studied shear dependent viscosities in polymer solutions. Little has been reported, however, on well-defined systems at shear rates above  $10^3$  reciprocal seconds. Pertinent studies at high shear are cited in references 1-5.

In this work, viscosities were measured on six cetane solutions of polyisobutene. Tests were made from 20-100°C. and at shear rates from  $5 \times 10^2$  to  $8 \times 10^6$  seconds<sup>-1</sup> using a concentric cylinder viscometer. Concentrated solutions of a linear polymer in a good solvent were chosen so that tests would yield large reversible viscosity changes due to shear. The viscosity of the solvent cetane, or *n*-hexadecane, was low and independent of shear over the range studied. It also has a high boiling point, 287.5°C., and can be readily obtained in good purity.

Reversible viscosity changes due to shear in laminar flow were correlated as a function of shear rate, shear stress, temperature, and polymer molecular weight and concentration. In earlier work on similar systems, irreversible viscosity changes were studied.<sup>6</sup> Irreversible viscosity losses resulted from polymer degradation at high shear.

## II. EXPERIMENTAL

The solutions tested were 11.5, 24.4, and 49.2 wt.-% polymer in *n*-hexadecane. Table I shows the polyisobutene connotation for each polymer used. Table I also gives the corresponding viscosity-average molecular weight calculated from an intrinsic viscosity of the polyisobutene in carbon tetrachloride at 30°C.<sup>7</sup> The method of compounding the cetane and carbon tetrachloride solutions has been described.<sup>6</sup> The polyisobutenes were kindly contributed by the Enjay Company. The cetane was a Du Pont petrochemical.

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A high shear, concentric cylinder viscometer was used. It was patterned after the design of Barber et al.<sup>6,8</sup> The nominal shear dimensions of the cylinders are 1 inch in diameter and 1<sup>7</sup>/<sub>8</sub> inches in length. The test fluid is held by surface tension between the cylinders. The inner cylinder is rotated, and the torques transmitted through the fluid are measured on the outer cylinder. Speeds of rotation are proportional to shear rate, and the resultant torques are a function of viscosity. Uncertainties in the temperature of the test fluid were kept below 1°C. by keeping the film thickness small and by the careful use of a thermostating liquid on both of the concentric cylinders. The measurement of Newtonian viscosities at high shear on low

TABLE I  
Viscosity Average Molecular Weight of Polyisobutene

Polyisobutene specification	Intrinsic viscosity	Molecular weight
MS	0.39	$4.0 \times 10^4$
MH	0.53	$6.2 \times 10^4$
120	5.9	$2.2 \times 10^6$

molecular weight polyethylenes and other fluids confirmed the absence of temperature gradients in the test fluid. Three inner cylinders of different dimensions, clearances  $1-15 \times 10^{-4}$  inches, were used to measure viscosities of polyisobutene solutions. The cylinders gave consistent data. Their shear rate ranges partially overlap. Measurements at each temperature were taken in order of both increasing and decreasing rate of shear. The data were reproducible and independent of the order in which measurements were taken except where polymer degradation occurred.<sup>6</sup>

The presence of laminar flow in the test film was confirmed by (1) the low Reynold's numbers involved, which were generally below one,<sup>9</sup> and (2) the equation of Taylor, which predicts speeds at which turbulence develops in rotational viscometers.<sup>10</sup> It is believed that viscosity and shear rate

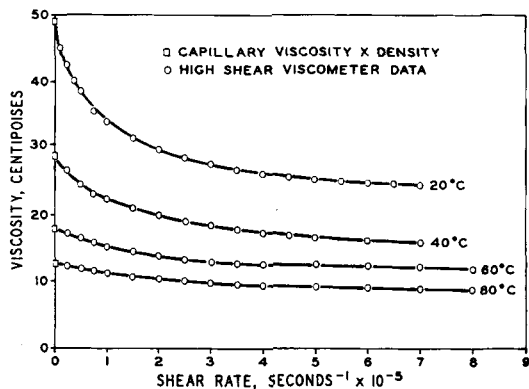


Fig. 1. Viscosity of 11.5% polyisobutene in cetane. Polymer molecular weight =  $6.2 \times 10^4$ .

measurements were good to about  $\pm 2\%$  of true values.

Molecular orientation times did not influence results as solutions were sheared for many seconds at each shear rate.<sup>11,12</sup> Thixotropy was never observed, although it has been reported by Bestul for similar solutions.<sup>13</sup>

### III. RESULTS

Figure 1 shows the change of apparent viscosity with shear rate and temperature for a 11.5% solution of polyisobutene, molecular weight  $6.2 \times 10^4$ . Conventional capillary viscosities were measured on this solution at each test temperature. The values, converted to centipoises, are plotted near the ordinate. Viscosity was essentially constant from capillary shear rates up to  $10^3 \text{ sec}^{-1}$ . The major changes in viscosity due to shear occurred between  $10^4$  and  $6 \times 10^5 \text{ sec}^{-1}$ . Polymer orientation apparently occurred predominantly within these limits. Solution viscosities became insensitive to shear rate as the test temperature was increased. The polymer contribution to viscosity at  $80^\circ\text{C}$ . was nearly independent of shear over the region investigated. This implies that at high temperature the existing shear stresses were not sufficient to cause significant polymer deformation and orientation.

Results, comparable to those in Figure 1, were obtained on a 11.5% cetane solution of the lowest molecular weight polyisobutene. These data are given in Figure 2. Figure 2 also shows viscosity changes with polymer concentration. Non-Newtonian flow was more pronounced and took place at lower shear rates at higher polymer concentrations. This corresponded to conditions of higher shear stress. The curves for the highest concentration, 49.2% polymer, terminate at stresses which induced polymer degradation.

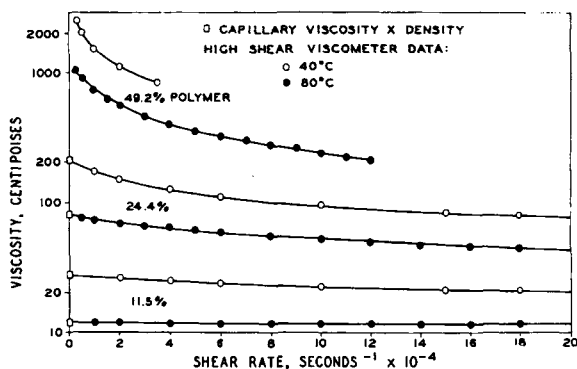


Fig. 2. Viscosity of concentrated solutions of polyisobutene in cetane. Polymer molecular weight =  $4.0 \times 10^4$ .

The data in Figure 2 have been used to evaluate the relationship between polymer concentration and viscosity. Plots of log viscosity vs. log concentration at constant shear stress showed curvature towards high viscosity over the range of measurement. The same coordinates showed a similar curvature for data at constant shear rates from  $5\text{--}30 \times 10^3 \text{ sec}^{-1}$ . As the shear rate was increased further, the curves decreased in slope and finally became effectively linear with identical slopes at 40, 60, and  $80^\circ\text{C}$ . At  $3 \times 10^4$  and  $12 \times 10^4 \text{ sec}^{-1}$ , viscosity was found to increase as the 2.5 and 2.0 power of wt.-% polymer. At low shear, the exponent is reported to be 5.0 for low solution concentrations of high molecular weight polyisobutene.<sup>5</sup>

Figure 3 gives viscosity-shear stress data for a 11.5% cetane solution of polyisobutene, molecular weight  $2.2 \times 10^6$ . Shear stress is used as the abscissa rather than shear rate because the viscosity dependence on shear rate was markedly greater than that shown in Figures 1 and 2. Capillary

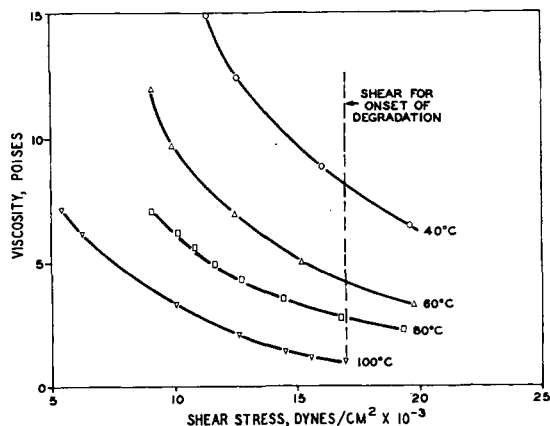


Fig. 3. Viscosity of 11.5% polyisobutene in cetane. Polymer molecular weight =  $2.2 \times 10^6$ .

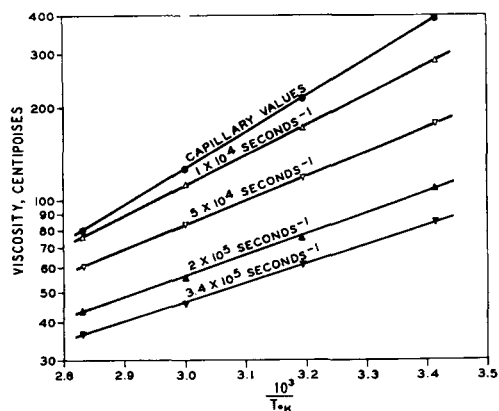


Fig. 4. 24.4% Polyisobutene in cetane at constant shear rates. Polymer molecular weight =  $4.0 \times 10^4$ .

viscosity measurements were not reported for this system as they are undoubtedly dependent on shear.<sup>5</sup> At 40°C. the viscosity of this system in Figure 3 changed 5 poises over the narrow and low shear rate range from 750 to 1000 sec.<sup>-1</sup>. At shear rates above about 10,000 sec.<sup>-1</sup> at 40°C., resultant shear stresses caused the rupture of polymer molecules in this solution. Results obtained at stresses above  $1.7 \times 10^4$  dynes/cm.<sup>2</sup> have thus been interpreted in terms of permanent rather than reversible viscosity changes.<sup>6</sup>

The variation of viscosity with temperature was evaluated by several shear correlations. Comparisons at constant shear rate indicate that data in Figures 1-3 are linear on a plot of log viscosity vs. reciprocal of absolute temperature. Typical results are shown in Figure 4 for a 24.4% solution of polyisobutene, molecular weight  $4.0 \times 10^4$ . Data on all solutions were obtained at four temperatures and interpreted at a series of shear rates. In most cases, data also fit this Arrhenius-type correlation when viscosities were compared at constant shear stress. The slopes of plots at constant shear rate and shear stress were the same in the region of low shear, Newtonian flow, but differed greatly in the range of shear dependent viscosities. Slopes measured at constant shear rate never exceeded those measured at constant shear stress.<sup>14</sup> Flow activation energies were obtained from these experimental slopes, see Figure 4, by simply multiplying by 2.303 times the gas constant.

Plots of log viscosity vs.  $1/T$  at constant shear rate were more nearly linear for all data than plots of log viscosity versus  $1/T^2$ . This latter correlation has been successfully used by others in interpreting data on polyisobutene systems.<sup>15,16</sup> It gave approximately linear relationships for some of these

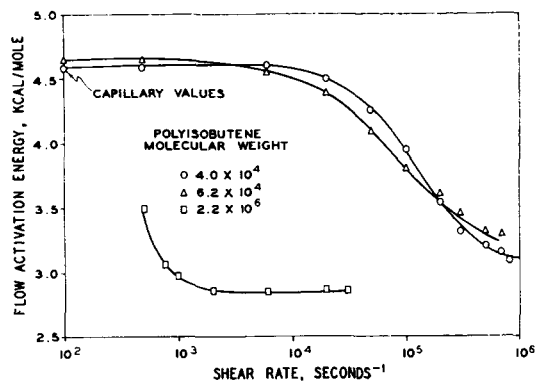


Fig. 5. Flow activation energies for 11.5% polyisobutene in cetane.

data. However, the  $1/T$  correlation was used throughout this work. This was because of the greater linearity of data and the merit in evaluating flow activation energy at constant shear rate,  $\Delta E_r^*$ . Bestul reports that certain bulk polyisobutenes also follow the  $1/T$  rule.<sup>14</sup> For a molecular weight of 70,000, activation energies of 5.9 and 3.5 kcal. were found at 200 and 2000 reciprocal seconds.<sup>14</sup>

Figure 5 shows the change of  $\Delta E_r^*$  with shear rate for three 11.5% cetane solutions of polyisobutene which differed only in polymer molecular weight. Activation energies changed with shear rate as stresses induced non-Newtonian flow. The change in  $\Delta E_r^*$  with shear rate was over 50% for the two lower molecular weight polymer solutions. For the highest molecular weight solution in Figure 5,  $\Delta E_r^*$  was found to be approximately constant over a shear rate range where non-Newtonian flow was strongly exhibited.

The low shear flow activation energies for the two lower molecular weight 11.5% solutions are within 1% of each other. The difference is not experimentally significant, although the order is as expected from molecular weights. An insensitivity of  $\Delta E_r^*$  to polymer molecular weight at low shear has foundation in theory and has been confirmed experimentally by Fox and Flory on similar systems.<sup>17</sup> At high shear rates,  $\Delta E_r^*$  also appears to be insensitive to polymer molecular weight. Constant activation energies are observed in Figure 5 for the highest molecular weight 11.5% solution as shear stress is increased into the region of polymer degradation.<sup>6</sup> Moreover, all solutions in Figure 5, irrespective of molecular weight, appear to approach a common  $\Delta E_r^*$  at high rates of shear.

The low shear, Newtonian  $\Delta E_r^*$  for the highest molecular weight 11.5% solution is equal to or greater than 7.8 kcal., the value measured on this

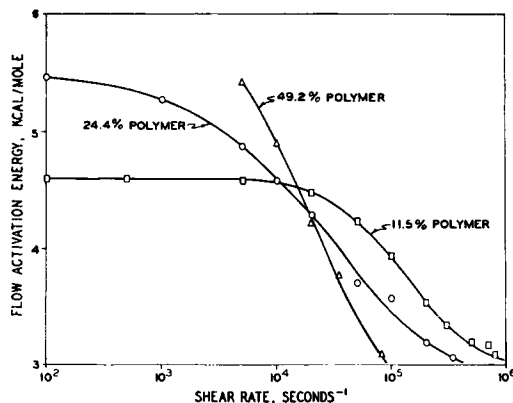


Fig. 6. Flow activation energies for cetane solutions of polyisobutene. Polymer molecular weight =  $4.0 \times 10^4$ .

system at constant shear stresses near  $1.5 \times 10^4$  dynes/cm.<sup>2</sup>. At this stress, the  $\Delta E_r^*$  for the lowest molecular weight 11.5% solution was equal to its low shear Newtonian value. Flow activation energies at constant shear stress showed the same type of change with shear as shown in Figure 5. They began to deviate from Newtonian values above  $10^4$  dynes/cm.<sup>2</sup>. At low shear,  $\Delta E_r^*$  increased with polymer concentration. The effect of concentration became less as measurements were made at successively higher rates of shear. Figure 6 shows that at between  $1-2 \times 10^4$  sec.<sup>-1</sup>,  $\Delta E_r^*$  is approximately the same for all concentrations tested. At still higher rates of shear, the order is reversed, with the highest concentration having the lowest  $\Delta E_r^*$ . Each curve in Figure 6 is S-shaped, indicating a tendency towards a constant  $\Delta E_r^*$  at both high and low rates of shear. The limiting dependence of  $\Delta E_r^*$  on concentration at high shear rates is difficult to determine from data.

High shear viscosities were also measured on the solvent, cetane. Viscosities and activation energies for cetane were found to be independent of shear rate from capillary values up to  $10^6$  sec.<sup>-1</sup>. Therefore, changes in viscosity and flow activation have been attributed solely to the effect of polymer.

#### IV. DISCUSSION

##### Flow Activation Energy

From the theory of rate processes,<sup>18</sup> Bestul has derived an equation for flow activation energy at constant shear rate.<sup>14</sup> This is the only expression available for estimating  $\Delta E_r^*$  at high rates of shear. By this equation  $\Delta E_r^*$  decreases with increasing shear stress as a function of molecular volume. Effective molecular volumes have been calculated from this equation for 10 and 25% decreases in

$\Delta E_r^*$  for a 11.5% solution of polyisobutene, molecular weight  $6.2 \times 10^4$ . These molecular volumes were 5.1 and  $1.8 \times 10^{-18}$  cc./molecule. The difference between values indicates that experimentally  $\Delta E_r^*$  decreased more rapidly than predicted by Bestul's equation. The molecular volumes from rate theory are also greater by a factor of 10 than those calculated from molecular weight and density of bulk polymer. A further problem with the equation for  $\Delta E_r^*$  is that it cannot accommodate experimental data above the points of inflection in Figures 5 and 6.

##### Polymer Molecular Weight

Data on 11.5% polymer solutions were used to study the variation of viscosity with polymer molecular weight. Log-log plots at constant shear rate were found to be linear with identical slopes at 40 and 80°C. This linearity and the temperature independence of slope is consistent with data previously reported at low shear rates where high polymer systems uniformly gave a slope of 3.4.<sup>19,20</sup> In this work, it was found that slopes decrease markedly with increasing shear rate. The values at  $10^3$  and  $10^4$  sec.<sup>-1</sup> were 1.1 and 0.7 for the slopes of log viscosity vs. log molecular weight.

Based on the viscosity of the low molecular weight solutions and an assumed slope of 3.4, the low shear viscosity of the highest molecular weight 11.5% solution was approximately  $10^3$  poises at 40°C. Thus, for this system at  $10^4$  sec.<sup>-1</sup>, over 99% of the polymer contribution to viscosity was reversibly lost.

##### Shear Stress

Reduced specific viscosities are reported by Horowitz to superimpose and decrease linearly when plotted against log shear stress.<sup>4</sup> This interpretation has been used on these data. At the highest temperatures, the decrease in viscosity with shear was less than that required for superposition of data. A given shear stress was apparently less effective in producing polymer orientation at higher temperatures where Brownian movement was more pronounced.

A reduced viscosity correlation, similar to that of Horowitz, has been presented by De Witt et al.<sup>5</sup> The major difference is that the latter involves a dependence on absolute temperature and upon the conditions of a reference state. Using a modified De Witt correlation, see Figure 7, all data from 20-80°C. on the two lower molecular weight solutions satisfactorily superimposed. This test was not applied to the highest molecular weight poly-

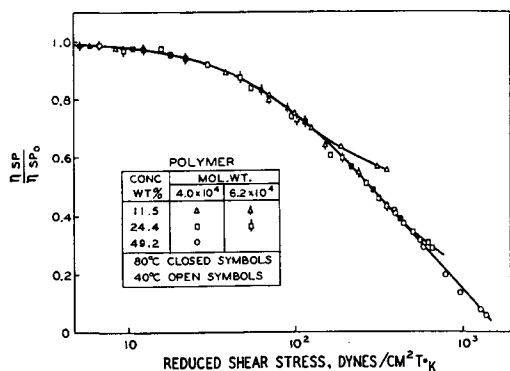


Fig. 7. Solutions of polyisobutene in cetane. Reduced variable correlation.

mer solution because of uncertainty in its low shear viscosity.

Curvature was found in all reduced viscosity correlations at shear stresses where non-Newtonian flow was incipient and where the maximum change of viscosity with shear was approached. It appears that the relationships presented by others<sup>4,11</sup> relating viscosity, fluidity, or polymer contribution to viscosity with shear rate or shear stress should show curvature for these conditions.<sup>21</sup> It is true, however, that somewhat more abrupt changes with shear may be expected for highly fractionated polymer systems. For the solutions tested, the solvent viscosity was low and independent of shear. Therefore, effectively the same reduced viscosity curves were obtained when the total viscosity was used rather than either specific viscosity or polymer contribution.

Plots of log viscosity or fluidity vs. log shear stress were linear for all data obtained on the highest molecular weight 11.5% solution. Equivalent results have been previously obtained on highly viscous materials.<sup>22</sup> Approximately parallel slopes were given by data at temperatures from 40–100°C. This linear correlation also held for the lower molecular weight 11.5% solutions. However, these plots became nonlinear at shear stresses below  $2 \times 10^4$  dynes/cm.<sup>2</sup> where Newtonian flow was approached.

For the highest molecular weight 11.5% solution, viscosity decreased with the 1.5 power of shear stress. For the lowest molecular weight solution of the same concentration, the exponent was about 0.3.

### Polymer Concentration

The reduced viscosity correlations of De Witt and Horowitz agree on the relationship between polymer concentration and non-Newtonian flow.<sup>4,5</sup>

Each illustrates that reduced viscosities superimpose when plotted as a function of shear stress divided by polymer concentration. Above 8% polymer, however, De Witt finds that the concentration dependence becomes somewhat different.<sup>5</sup>

All concentrations tested in this work were above 10 wt.-% polymer. From these data it was concluded that reduced viscosity correlations could be made independent of polymer concentration. Figure 7 illustrates the superposition of reduced viscosities at 40 and 80°C. for three concentrations from 11.5–49.2% polymer. Concentration became a factor only beyond the points of inflection in Figure 7. In this region the mechanism responsible for non-Newtonian flow was approaching saturation. This master curve is thus followed to the highest stresses for data at the lowest temperatures and for solutions containing the highest polymer molecular weight and concentration.

Figure 7 indicates that a reduced viscosity vs. log (shear stress/ $T^\circ$ K) correlation may be used to superimpose the three variables of polymer molecular weight, concentration, and temperature. The correlation is good for all systems for which reduced viscosities could be derived. This includes the two lower polymer molecular weights, 4.0 and  $6.2 \times 10^4$ ; at three concentrations, 11.5, 24.4, and 49.2 wt.-% polymer; and at five temperatures from 20–80°C. Either total or polymer contribution to viscosity may be used. The coordinates suggested involve neither a reference state nor a term for polymer concentration.

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### Synopsis

A concentric cylinder viscometer was used to measure high shear viscosities of polyisobutene solutions. Data were obtained in laminar flow from 20–100°C. and at shear rates from  $5 \times 10^2$  to  $8 \times 10^5$  sec.<sup>-1</sup>. Three polymer molecular weights,  $4.0 \times 10^4$ – $2.2 \times 10^6$ , in three concentrations from 11.5–49.2 wt.-% polymer were tested in cetane. The viscosity of cetane at all test temperatures was low and independent of shear rate up to  $10^6$  sec.<sup>-1</sup>. Therefore, variations in viscosity with shear were due totally to the effect of polymer. Viscosities of 11.5% solutions of low molecular weight polyisobutene,  $4\text{--}6 \times 10^4$ , approached limiting viscosities at both high and low rates of shear. Viscosity changed markedly between the limiting values as did the flow activation energy at constant shear rate,  $\Delta E_r^*$ . At extremes of both high and low shear rate  $\Delta E_r^*$  appeared to be insensitive to polymer molecular weight. Solutions containing the highest molecular weight and concentration of polyisobutene reached shear stresses for polymer degradation before a limiting high shear viscosity could be observed. For all solutions,  $\Delta E_r^*$  was independent of temperature from 20–100°C. At low shear,  $\Delta E_r^*$  increased with polymer concentration. At high shear, the concentration dependence was reversed, with the highest concentration having the lowest  $\Delta E_r^*$ . A simple shear correlation was found to superimpose all data for which reduced viscosities could be derived. Reduced specific viscosities superimposed on a master curve when plotted against log (shear stress/ $T^\circ K$ ). The correlation covered data at all temperatures and concentrations for the two lower molecular weight polymer solutions.

### Résumé

On utilise un viscosimètre à cylindre concentrique pour mesurer les viscosités à tension de cisaillement élevée de solutions de polyisobutène. On a obtenu des résultats d'écoulement laminaire de 20 à 100°C et à des tensions de cisaillement de  $5 \times 10^2$  à  $8 \times 10^5$  secondes<sup>-1</sup>. On a essayé trois polymères de poids moléculaires  $4.0 \times 10^4$ – $2.2 \times 10^6$ , à trois concentrations en poids pour cent variant de 11.5 à 49.2% dans le cétane. La viscosité du cétane à toutes les températures était faible et indépendante de la tension de cisaillement jusque  $10^6$  secondes<sup>-1</sup>. Les variations de viscosité en fonction du cisaillement étaient donc dues entièrement à l'action du polymère. Des viscosités de solutions à 11.5% de polyisobutène de bas poids moléculaire ( $4\text{--}6 \times 10^4$ ), tendent vers des viscosités limites tant aux hautes qu'à faibles tensions de cisaillement. La viscosité change de façon appréciable entre ces valeurs limites de façon analogue

à l'énergie d'activation d'écoulement,  $\alpha E_r^*$ , à tension de cisaillement constante.  $\Delta E_r^*$  semble être indépendante du poids moléculaire du polymère aux hautes et basses tensions de cisaillement limites. Les solutions contenant du polyisobutène de poids moléculaires et de concentrations les plus élevées atteignent des tensions de cisaillement pouvant provoquer une dégradation du polymère avant que la viscosité limite pour les hautes tensions de cisaillement ne puisse être observée. Pour toutes les solutions  $\Delta E_r^*$  était indépendante de la température dans un domaine de 20 à 100°C. A faible vitesse de cisaillement  $\Delta E_r^*$  croît en fonction de la concentration en polymère. A haute tension de cisaillement par contre,  $\Delta E_r^*$  décroît en fonction de la concentration. Une corrélation simple du cisaillement a été trouvée; elle se superpose à toutes les données pour lesquelles des viscosités réduites peuvent être dérivées. Les viscosités spécifiques réduites se superposent sur une abaque lorsqu'on porte le logarithme de la tension de cisaillement en fonction de la température absolue. La corrélation s'étend aux données obtenues à toutes les températures et concentrations pour les deux solutions des polymères de plus bas poids moléculaires.

### Zusammenfassung

Ein Viskosimeter mit konzentrischen Zylindern wurde zur Messung der Viskosität von Polyisobutenlösungen bei hoher Scherung verwendet. Versuchsergebnisse bei laminarem Fließen wurden im Temperaturbereich von 20–100°C und bei Schergeschwindigkeiten von  $5 \times 10^2$  bis  $8 \times 10^5$  sek<sup>-1</sup> erhalten. Drei Polymermolekulargewichte,  $4,0 \times 10^4$ – $2,2 \times 10^6$ , wurden bei drei Konzentrationen im Bereich von 11,5–49,2 Gewichtsprozent Polymeres in Cetan untersucht. Die Viskosität von Cetan war bei allen Versuchstemperaturen niedrig und bis zu  $10^6$  sek<sup>-1</sup> von der Schergeschwindigkeit unabhängig. Die Abhängigkeit der Viskosität von der Scherung war daher zur Gänze dem Einfluss des Polymeren zuzuschreiben. Die Viskosität von 11,5% Lösungen eines Polyisobutenes mit niedrigem Molekulargewicht,  $4\text{--}6 \times 10^4$ , erreichte sowohl bei hoher als auch bei niedriger Schergeschwindigkeit einen Grenzwert. Die Viskosität sowie die Aktivierungsenergie des Fließens bei konstanter Schergeschwindigkeit,  $\Delta E_r^*$ , zeigten zwischen den Grenzwerten merkliche Änderungen. Im Extremfall schien  $\Delta E_r^*$  sowohl für hohe, als auch niedrige Schergeschwindigkeit gegen das Molekulargewicht des Polymeren unempfindlich zu sein. Lösungen, welche die höchsten Molekulargewichte und Konzentrationen von Polyisobuten enthielten, erreichten Schubspannungen, die zum Abbau des Polymeren führten, bevor ein Viskositätsgrenzwert für hohe Scherung beobachtet werden konnte. Bei allen Lösungen war  $\Delta E_r^*$  zwischen 20 und 100°C von der Temperatur unabhängig. Bei niedriger Scherung nahm  $\Delta E_r^*$  mit der Polymerkonzentration zu. Bei hoher Scherung war die Konzentrationsabhängigkeit umgekehrt und die höchste Konzentration hatte das niedrigste  $\Delta E_r^*$ . Für alle Ergebnisse, die eine Ableitung reduzierter Viskositäten erlaubten, ergab sich eine einfache Scherungskorrelation. Beim Auftreten gegen log (Schubspannung/ $T^\circ K$ ) lieferten die Werte der reduzierten, spezifischen Viskosität einen einheitlichen Kurvenzug. Die Korrelation war für die Ergebnisse an den Lösungen der beiden niedrigeremolekularen Polymeren bei allen Temperaturen und Konzentrationen gültig.

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