

## On Some Rheological Phenomena of Amorphous Polymers

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### Synopsis

The molecular domain model for flexible macromolecules is presented in brief, and various observations are enumerated, indicating that the model holds true for the solid, melt, and solutions of different concentrations. The four forms in which the domains can exist under shear stress are then presented, and, by referring to them, such rheological phenomena as "die swell," sudden jumps in flow rate, critical concentrations, and changes in viscosity are qualitatively explained.

### INTRODUCTION

It was recently proposed<sup>1</sup> that linear nonionic amorphous polymeric molecules exist in the form of molecular domains. Accordingly, each molecule fills a volume approximating a spheroid in which the distribution of the segmental density is about uniform. Only at the domain surface the segmental density drops sharply. Interdomain interactions are limited to intersurface interactions of transitory or permanent character. In a subsequent paper, it was shown that the brittle-ductile relationship in amorphous polymers can be explained on the basis of the same model.<sup>2</sup>

Employing the same molecular domain model, we shall attempt in this paper to give qualitative explanations to a few rheological phenomena encountered in polymeric melts and solutions.

### DISCUSSION

It is well known that with respect to flow characteristics, even relatively short flexible chain molecules, with molecular weights around 20,000, approach the behavior of impenetrable coils.<sup>3</sup> This is, of course, expected from our model. According to the model, the volume occupied by the molecular domain changes over three ranges of solution concentration. In the solid or melt, the domains are of a volume corresponding to the amorphous density of the polymer at that temperature. As they are

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deformable spheroids, they impinge on one another and fill the space, and the occupied volume is almost the same as the domain's volume. In the concentrated or semiconcentrated solution, the volume taken up by the molecular domain tends toward four times its volume in the melt. This ratio of occupied space to domain volume is due to excluded volume effects and not to significant swelling of individual domains. Such ratios were reported by Maron and co-workers<sup>4,5,6</sup> and by Graessley.<sup>7</sup> In such solutions, the molecular domains are far more compact than the occupied volumes calculated on the basis of random coils<sup>8</sup>. Upon dilution, the occupied volume does not change much over a range from very concentrated solution down to a polymer volume fraction of around 0.04. This independence from concentration was shown to hold by various means such as vapor pressure determination,<sup>4,6</sup> flow behavior,<sup>9</sup> light scattering,<sup>10</sup> and diffusion of polymer solute through low molecular weight  $\theta$ -solvent.<sup>11</sup>

At polymer volume fraction lower than 0.04, the molecular domains start swelling up, with a concomitant increase in the occupied volume.<sup>4,6,12</sup> Even though the molecular domains expand greatly in size, they retain rather well-defined surface regions across which the macromolecular segmental density drops from the core value to practically zero. We believe that the uniform thickness of adsorbed polystyrene (PS) layers, reported by Stromberg and co-workers,<sup>13-16</sup> and the incremental addition of equally thick subsequent layers indicate that the polymer molecules are being adsorbed from the dilute solutions not as random coils but as well-formed molecular domains. GPC studies of adsorption of poly(vinyl chloride) (PVC) have led Felter<sup>17</sup> to similar conclusions regarding the shape of the adsorbed molecular species. Bromination of natural rubber molecules in very dilute solutions with subsequent electron microscopy showed that natural rubber molecules in dilute solutions exist in the shape of well-formed spheroids.<sup>18</sup> Molecules of cellulose nitrate, polycarbonate, and PS in very dilute solutions were also shown to exist in spheroid shape.<sup>19</sup>

In very concentrated solutions, the domain characteristics are retained. This was elegantly shown by selectively graft polymerizing the surfaces of such domains in highly concentrated solutions and in the gel state.<sup>20</sup> An observation<sup>21</sup> relating the critical dosage of irradiation for gel formation to molecular weight is explainable on the basis of the domain model: the smaller the molecule, the larger its relative surface area and, hence, the smaller will be the critical dosage for gelation.

Upon reaching the solid state, the amorphous polymers retain their domain structure. Now the domains are compressed one against the other and, due to their deformability, fill the available space. Still, the interdomain interactions are largely intersurface ones. The existence of the domains in the solid is evidenced from the existence of nodules.<sup>1</sup> These are either monomolecular domains or multimolecular aggregates. Other correlations are, for example, the model for deforming network in elastomers, similar to the interdomain interactions, derived by Ziabicki,<sup>22</sup> and the fact that there exist two stages in the formation of effective network upon crosslinking natural rubber<sup>23</sup>

Even though amorphous, the molecular domains can possess varying measures of internal order. This is, most probably, the case with the amorphous nodular structures in the solid. The mere observation of nodules by darkfield electron microscopy is a strong proof that there is some order within the solid-state nodule. Such ordering can easily be effected also in solution by, say, partially orienting intradomain segments in the flow direction. It was actually shown that there exists an amount of internal order in PS and poly(vinyl acetate) lattices,<sup>24</sup> in PVC and poly-(methyl methacrylate) (PMMA) precipitated from solution,<sup>25</sup> and even in molten polyethylene (PE).<sup>26</sup> A most obvious result of segmental ordering within the domains is the flow birefringence in the concentrated solution and in the melt.

Under theoretical  $\theta$ -conditions, the polymeric domains start precipitating from solution. Within the domain, the segmental density approximates that which exists in the precipitated solid, but each domain still occupies about four times its volume. The excess occupied volume in the solution is due to two factors: firstly, the packing of mutually excluding spheroids leads to a large excluded volume, and, secondly, each domain is thermally mobile and precludes other domains from occupying with it a volume significantly larger than itself. According to excluded volume theories, the excluded volume per domain is four times its volume.<sup>27</sup> When the conditions are not theoretical  $\theta$ , surface segments interact with the solvent, extend away from the surface, and make the excluded volume per domain larger than the expected fourfold its actual volume. Hence, an increase in occupied volume takes place with improved polymer-solvent interaction merely by a very small fraction of the domain's mass being extended as loops or end strands far beyond the confines of the domain spheroid. A polymer-solvent interaction, leading to different occupied volumes, was shown experimentally to exist,<sup>4,10</sup> indicating that experimental  $\theta$ -conditions cover a whole range of conditions around the theoretical  $\theta$ -conditions.

A decrease in the occupied volume, below fourfold the domain volume, can take place under conditions where polymeric domains are effectively segregated out of the solvent and aggregate together, deforming and penetrating into the excluded volume of each other. Such a decrease<sup>6</sup> and segregation<sup>28</sup> were shown to exist in concentrated solutions and in  $\theta$ -conditions, respectively. A schematic representation of the occupied volume as a function of volume fraction is given in Figure 1.

All the aforementioned observations, either unexplainable or unsatisfactorily explained on the basis of homogeneous segmental distribution in the solution which is, in turn, a consequence of the random coil and entanglement theories, are predicted from the molecular domain model and are explained by it.

We have established, therefore, that in the solid, melt, concentrated, and semiconcentrated solutions, and to a lesser extent in the dilute solution amorphous, linear, flexible nonionic macromolecules exist in molecular domain form. Having established this, we shall show how this model qualitatively explains some rheological properties of such polymers.

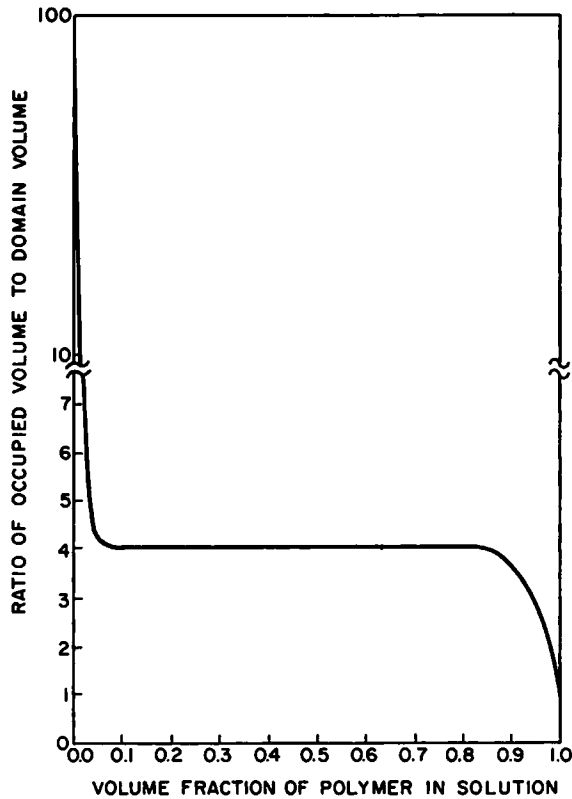


Fig. 1. Occupied volume as a function of volume fraction of polymer in solution.

Under stressed flow conditions, the molecular domains are not completely rigid but show a varying degree of deformation. This deformation is opposed to by the intramolecular uniform segmental distribution and the corresponding Lennard-Jones-type intersegmental forces. Hence, if the duration of flow under deformed conditions is longer than the maximum relaxation time for the particular segment at a given temperature, then that segment, and in a similar manner the whole domain, will relax and conform to the stress-imposed shape and reach a new point of metastable energy minimum in the new shape. Under these conditions the molecule will not return to its initial shape unless supplied with sufficient energy to overcome the activation energy barrier involved. In the subsequent paragraphs, the flow characteristics will be treated for conditions in which the long-range relaxations do not take place, that is, in flow through not "too long" tubes or at "too high" temperatures.

Under melt flow conditions, the molecular domains can exist in four forms. These are schematically presented in Figure 2. The transition from one form to another depends on the following parameters: the chain rigidity, availability of space to be occupied by the segments, temperature, local stress, and the duration at a given temperature or under a given

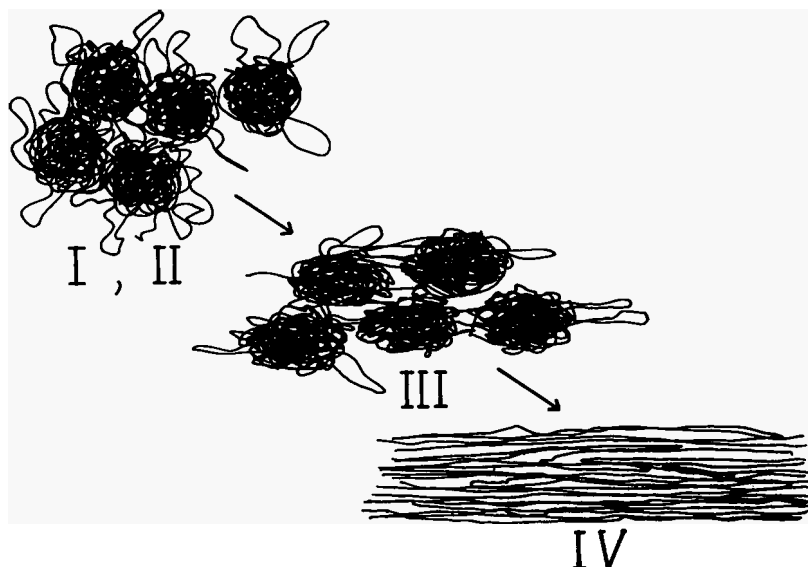


Fig. 2. Schematic representation of the four forms of molecular domains under shear stress.

In form I, the molecular domains are spheroids, with some permanent but mostly transitory interdomain interactions. The differentiation between permanent and transitory interactions is temperature, frequency, and solvent dependent. The ratio of transitory to permanent interactions increases with increasing temperature or dilution, but decreases with increased frequency.

Under flow conditions above  $T_g$ , the existing free volume within each domain facilitates some segmental motion and domain deformability. Yet, due to the characteristic chain stiffness and to the metastable Lennard-Jones-type energy well in which each segment is, a certain resistance to the deformation of the molecular domains would exist. This resistance is typical of each polymer. Below  $T_g$ , with the segmental mobility much more constrained, the resistance to domain deformation will be much higher. Such deformations are, however, not precluded and do take place, e.g., in cold-drawing.

Above  $T_g$ , the thermal motions of the segments makes them more flexible and the deformation of whole domains much easier. When a molecular domain is easily deformable, but a spheroid yet, we say it is in form II. Dissolution of polymer in low molecular weight solvent brings about the same result. With enhanced deformability, the interdomain surface interactions will gradually decrease in significance while deformation phenomena will become more important. Also, the easily deformable

domains will tend less to regain their initial shape once deformed by an external force.

Under ever-increasing shear rates, the domains undergo three simultaneous processes. Firstly, the domains gradually change from spheroids to ellipsoids whose long axes are in the direction of flow. Within the ellipsoid, a higher degree of segmental orientation in the flow direction is created, merely by the elongation of the whole domain in that direction. Secondly, by virtue of the deformation there would be less domain rotation and tumbling in the flow direction. Thirdly, under the higher shear rates, loops and strands will extend less from the domain surface than under low shear conditions. There would be, therefore, increasingly less interdomain interaction efficiency, and regeneration of broken interactions. At this stage, the domain is in form III.

With increasing shear, the long axis of the ellipsoid will elongate at the expense of the decreasing cross section of the domain. Yet, as long as there are a few intradomain segments parallel to one another, they will gradually relax upon removal of the shear forces, and the domain will revert to its spheroidal metastable equilibrium position.

At extremely high shear rates, the domain elongates so much that a point is reached at which, if it does not rupture, the molecule assumes the overall shape of a long chain more or less stretched in the flow direction, with practically no intradomain parallel segments. We term this as form IV. Once the domain is in such an extended form, chain slippage becomes very facile, and a dramatic increase in flow rate should be observed. As under these conditions interdomain interactions that are molecular weight dependent are eliminated, the viscosity of the polymer in form IV drops to a very low level, the level of very short and noninteracting chains, and becomes independent from molecular weight.

In solution, the transitions from one form to the other is more facile than in the melt. We should expect, therefore, that the transition to form IV will take place under lower shear rates than in the melt. If, however, the concentration of polymer in solution is lower than a certain volume fraction, then the sudden change in flow characteristics should not be observed. This volume fraction, termed "critical concentration," is the concentration at which the polymeric molecular domains cease touching one another and forming a continuous network held together by transitory interdomain surface interactions. As the occupied volume of the domains is about fourfold the actual domain volume,<sup>27</sup> the critical concentration below which the network falls apart should be about 0.25. Exact values of occupied volumes of some polymers semiconcentrated and concentrated solutions in different solvents were determined experimentally by Maron and co-workers<sup>4,5,6</sup> and are about fourfold the volume of the polymer molecules themselves. "Critical concentrations" of about 0.25, transforming to form IV at somewhat lower shear rates than the corresponding melts, were recently observed by Malkin and co-workers,<sup>29</sup> in agreement with our model's expectations.

Under zero shear conditions, molecular domains exist only in form I or form II. It was shown<sup>1</sup> that under these conditions for monodisperse polymers

$$\epsilon_t = K_1N + K_2N^{3/2} \quad (1)$$

where  $\epsilon_t$  is total interaction between molecular domains manifested as either zero-shear viscosity  $\eta_0$  or maximum relaxation time  $\tau_m$ ,  $K_1$  and  $K_2$  are constants; and  $N$  is a measure of the chain length. In the transition zone from low molecular weight fractions to high molecular weight fractions one has

$$N \leq x: K_1 > 0, K_2 = 0$$

changing over a fourfold increase in chain length to

$$N \geq 4x: K_1 = 0, K_2 > 0$$

under the condition

$$K_1 + K_2 = \text{constant.}$$

Upon dilution, the intrinsic viscosity is<sup>1</sup>

$$[\eta]_0 = QN^a \quad (2)$$

where  $Q$  is a constant and  $a \geq 1/2$  is exactly  $1/2$  under theoretical  $\theta$ -conditions. From the above consequences of the molecular domain model, it is obvious that non-Newtonian flow can occur in linear nonionic amorphous polymers only when  $N > x$ , in agreement with other observations.<sup>30,31</sup> Broad molecular weight distributions, having an extended range of  $\epsilon_t$ , will result in wide range of transitions<sup>32,33</sup> from form I to form II to form III.

In non-Newtonian flow under shear, when the domains are in form II or form III, the Eyring equation<sup>34</sup>

$$\eta = (\eta_0\omega P/kT)/\sinh(\omega P/kT) \quad (3)$$

holds under low-stress  $P$  for a single type of kinetic unit. In the equation,  $\eta$  is the viscosity,  $\omega$  is the volume of a kinetic unit of flow,  $k$  is Boltzmann's constant, and  $T$  is the temperature. When  $P$  increases, the equation changes into<sup>35</sup>

$$\eta = A \exp(U_0 - \omega P)/kT \quad (4)$$

that becomes more exact the greater  $P$  is. In this equation,  $A$  is a constant and  $U_0$  is the "zero" activation energy for flow. In both cases, the kinetic flow unit volume  $\omega$  seems to be that of the whole domain, the size of which is of the same order of magnitude determined<sup>36</sup> for the "Eyring flow volume" for a number of polymers.

Under form II conditions, one would expect the highest possible amount of "die swell" for each polymer at equal shear stress. That is, a less deformable domain will bounce back to its initial sphericity when the stress is

removed better than the same domain after being rendered easily deformable by further heating and enhanced segmental flexibility. Hence, a polymer whose segments were rendered sufficiently flexible not to fracture will manifest a large "die swell" at a temperature closer to  $T_g$  than at higher temperatures. On the other hand, some rather rigid molecular domains, in form I, hardly deform and, therefore, do not exhibit a large "die swell" upon the removal of stress. The relatively rigid PVC is typical. Generally, the "die swell" data contain many contradictory observations (compare, for example, references 37, 38, 39, and 40 for high-density PE) and most probably reflect the fact that at different temperatures the polymers exist in different forms and that there is a gradual change in behavior throughout the range of form II.

The molecular domain model indicates that the ratio of surface to core segments is larger for a small domain than for a large one. Thus, under the same shear rate, the core of the smaller domain will deform more than the core of the larger domain; and when the stress is removed, the smaller domain will revert faster to sphericity. Hence, under identical conditions, a narrow fraction of low molecular weight polymer (but where, in eq. (1),  $K_2 > 0$ ) will exhibit higher "die swell" than the higher fractions. Similarly, a broad-distribution sample containing low molecular weight fractions will exhibit larger "die swell" than a polymer with a narrower distribution. Such a behavior was found to exist in PS, PE, and polypropylene (PP).<sup>41,42</sup> The behavior described here will prevail until the domains will transform form III to form IV.

The point where flow mechanisms linked with enhanced domain deformability become the dominant ones, and interdomain interactions are relegated to secondary importance, is the point of transition from form I to form II. This transition is observable, for different polymers, above and below  $T_g$ . Under conditions of melt flow, we believe this transition to correlate with the  $T_{1,1}$  transition<sup>43</sup> and with the change in flow characteristics as manifested, for example, in the change in activation energy of flow.<sup>43-51</sup> In the solid state, we believe that the form I to form II transition is manifested by the change in slope of stress-strain curves of elastomers under small deformations at low temperatures<sup>52,53</sup>; in the different slopes of time to rupture versus stress at different temperatures<sup>54,55</sup>; and in the transition from linear to nonlinear viscoelastic behavior above and below  $T_g$ .<sup>56,57</sup> The drop in the coefficient of friction of, for example, low-density PE at around 60°C,<sup>58</sup> which is the  $T_{1,1}$  (PE) transition<sup>43</sup> is explainable on the basis of a transition from form I to form II of the amorphous component. The same explanation holds for the change in slope of shear stress versus rate of deformation of PIB solution.<sup>59</sup>

Because in form II the domain gradually increases its deformability while losing the transitory interdomain interactions, there is a gradual decrease in the viscosity of the polymer, with increased shear rate, throughout the range of form II. Once the interaction between the domains is reduced to practically only the overall friction due to the motion of one ellipsoid rela-



tive to the other, the domain is in form III. In this form, the viscosity is much lower than in form I and is yet shear and molecular weight dependent, but to a lesser extent. The same behavior will also hold true with respect to "die swell."

The phenomenon of "melt fracture" takes place at rather high shear rates where the polymer is well in form II and form III. It always takes place before the polymer reaches form IV. We believe that "melt fracture" represents macroconditions in the flow system, conditions leading to effects that could become apparent only when the interdomain interactions become sufficiently small. The macroconditions are mainly the large flow rate and shear rate gradients across the flow direction.<sup>60</sup> We shall not concern ourselves with "melt fracture" anymore.

In form IV, the polymer practically squirts out of the tube with a dramatically enhanced flow rate.<sup>41,61-67</sup> The change from form III to form IV is rather abrupt and occurs in the melt under shear stress of about  $5 \times 10^6$  dynes/cm<sup>2</sup>. The change is also manifested by a sharp drop in viscosity.<sup>68</sup> It is probable that the thermal runaway of nylon 610 during drawing under constant load<sup>69</sup> happens when the amorphous domains transform from form III to form IV. The suggestion of Vinogradov et al.<sup>68</sup> that the spurting under very high shear stress is due to the transition to the "high-elastic" state (that is, due to the formation of relatively stable intermolecular network) can hardly be reconciled with the experimental observations. As the same segmental mobility and time effects are manifested in both the intersegmental interactions and the disengagements, it seems highly improbable that the number and/or lifetime of interactions of a permanent nature will increase with shear stress at the expense of the temporary interactions. On the other hand, the lowered viscosity, sudden jump in flow rate, and possible molecular slippage between the bulk of the flowing mass and the very thin layer adhering to the wall of the tube can all be explained as due to domain shearing and molecular orientation in a rather extended form in the flow direction.

Finally and briefly, a comment concerning the initial modulus of high elasticity of polymeric solutions. It passes through a minimum at intermediate composition of blends of narrow molecular weight fractions. This peculiarity was observed in concentrated solutions of blends of the same polymer<sup>70</sup> and of similar ones.<sup>71</sup> Experimental data do not fit either the statistical random coil<sup>72,73</sup> or the hard sphere<sup>74</sup> approximations. We believe that the data indicate that small domains are being sheared by larger ones much easier than domains being sheared by others of the same size. As observed,<sup>71</sup> this enhances the elasticity of the solution but not its viscosity; the former is primarily dependent on shear of domains while the latter is more dependent on transitory interdomain surface interactions. The enhanced shearing and deformation of smaller domains by larger ones also contributes to the larger "die swell" of broad molecular weight distribution polymers as compared with narrow fractions of the same molecular weight under the same conditions.

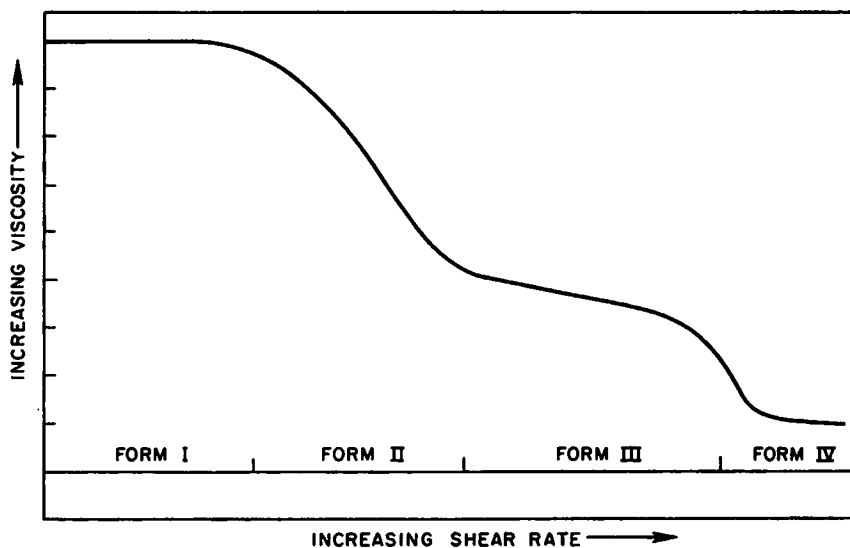


Fig. 3. Viscosity vs. shear rate and the four forms of molecular domains.

In conclusion it can be said that the molecular domain model, presented schematically in its four forms in Figure 2, explains some rheological phenomena of melts and solutions, such as "die swell," "critical concentration," sudden changes in flow rates, and viscosity. The relationship between domain form and viscosity is presented in Figure 3.

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