

Effect of Aggregation States on Some Properties of PVC Solids and Melts

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Synopsis

Plasticized compounds of poly(vinyl chloride) (PVC) have been prepared using PVC polymer as supplied and as recovered from solutions in tetrahydrofuran. Mechanical properties and melt elasticity measurements were found to vary significantly among these compounds. It is proposed that the solid-state characteristics and melt elasticity parameters in these compounds depend on the state of chain entanglement and that the entanglement state can be modified significantly by procedures such as used here. Annealing experiments have shown that the rates of attaining property equilibria—symptomatic of equilibrium entanglement states—are dependent on diffusion processes. Neither solution-modified nor control PVC compounds are in steady states when first tested; consequently, time-dependent property variations may be expected as morphological steady states are attained at conventional use temperatures for PVC compounds. The present study extends to PVC the principles of entanglement network modification through solution, or shearing processes, as a means of selecting preferred property balances in melt processing and mechanical properties. That principle had earlier been shown to apply to polyethylenes.

INTRODUCTION

In a recent publication,¹ we noted that, because of long relaxation times, the processing behavior of many commodity polymers is influenced by previous shear and thermal history. Similarly, mechanical and physical properties are often measured with polymers in metastable states, their entanglement network structures not having relaxed from perturbations caused by processing and thermal histories. A systematic investigation was launched to establish whether multivalued properties were general to commodity polymers, and to seek guidelines as to the magnitude and durability of effects which can be produced by controlled modifications of the entanglement morphology in a given polymer.

The present article summarizes results obtained in a study involving a mildly plasticized poly(vinyl chloride) (PVC) compound. The work closely parallels that reported in concurrent reports dealing with members of the polyethylene group.^{2,3} Polyethylenes, of course, are logical subjects for property modification, very high molecular weight chains frequently being involved, these giving rise to readily modifiable networks with high entanglement densities. In comparison, PVC molecular weights extend over a more limited range, and molecular weight distributions are also much

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narrower than those found in the polyolefin group. Compounds based on PVC were therefore appropriate candidates for a study which questioned the general applicability to polymers of network modification principles. As in the work with polyethylenes, the network structures in PVC were modified by abruptly precipitating the polymer from solutions. The procedure, though impractical from most industrial viewpoints, is able to produce appreciable modification to the polymer's aggregation state without the risk of thermal or mechanical degradation.⁴ It was therefore well suited for present purposes.

EXPERIMENTAL

Materials and Sample Preparation

A single PVC compound was used throughout this work. Its composition was as follows: PVC K-65 resin 100 phr; DnOP plasticizer 12.5 phr; tribasic stabilizer 3.0 phr.

For control purposes, a reference compound was based on the commercially available materials as supplied. In other experiments the PVC used for compounding was recovered from solutions in tetrahydrofuran (THF), a good solvent for this polymer with $\alpha = 0.65$ in the pertinent Mark-Houwink relationship.⁵ The polymer, dissolved at 30°C and at concentrations of 0.2% and 1.7% (w/v) was precipitated by the addition of excess H₂O, recovered and washed repeatedly with distilled water, and finally vacuum-dried at 50°C, 0.2 Torr for about 50 h. Internal reflectance IR spectra gave no indication of residual solvent entrapped in the polymer. The quantitative removal of solvent was further confirmed by microgravimetric measurements performed on PVC specimens recovered from THF solution. Weight constancy to $\pm 0.2\%$ was attained, generally within 30 h of drying by the procedure noted above. Further comment on the choice of initial polymer concentrations is offered in the Results section.

Compounding was done in a Brabender Plasticorder at 120°C and 40 rpm, mixing being continued to a steady torque reading (approx. 6 min). The blended materials were then compression-molded in a metallurgical press² at 120°C and $F > 5000$ psi. These blending and molding procedures produced cohesive test specimens at minimum temperature. In this manner the reentanglement of solution-modified polymer was inhibited, allowing for a more realistic evaluation of effects, particularly on the solid-state properties of the compounds.

Testing Procedures

Mechanical properties of PVC compounds were evaluated in stress-strain, using Instron test apparatus and test specimens shaped in accord with ASTM D638. The tester was operated at jaw separation speeds ranging from 0.5 to 20.0 cm · min⁻¹. All reported data are averages of five evaluations; test specimens were conditioned at 23°C, 50% RH for 24 h prior to data collection.

Dynamic mechanical properties were obtained with the Rheovibron apparatus at 11 Hz, and thermal responses of the compounds were measured

with a Perkin-Elmer DSC-2 scanning calorimeter. Certain of the mechanical properties were measured after systematic annealing of the PVC samples. Annealing experiments were performed at 45°C, 60°C, 80°C, and 100°C, in air ovens, but with the specimens placed in desiccators blanketed with dry N₂. Annealing times were limited to 100 h in order to avoid any possibility of polymer thermal degradation.

Annealed samples were examined for any traces of discoloration and random samples were cut for IR scanning. These procedures showed no evidence of chemical change resulting from annealing exposures.

Finally, in a limited number of experiments, the apparent melt viscosity and elasticity of PVC samples was determined using a gas-driven capillary rheometer. Melts were extruded at 190°C, through a capillary die with $L/R = 9.95$. Melt elastic behavior was characterized by the extrudate swelling parameter B defined by

$$B = D/D_0 \quad (1)$$

where D and D_0 , respectively, are the diameters of the extruded polymer rod and the capillary die.

RESULTS AND DISCUSSION

Solution Properties

The initial polymer concentration from which PVC samples were recovered was selected from reduced viscosity plots, as shown in Figure 1. A significant deviation from the linearity evident at lower concentrations occurs when $c > 1.1 \text{ g} \cdot \text{dL}^{-1}$. It is proposed that at lower concentrations the polymer chains approach molecular dispersion states, while, in the nonlinear region in Figure 1, more highly aggregated solute states are

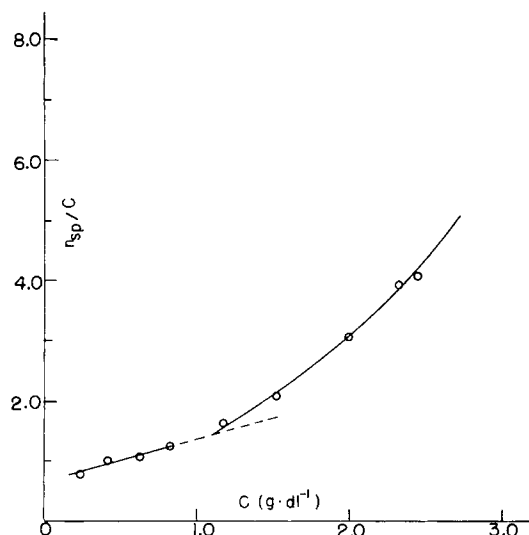


Fig. 1. Specific viscosity-concentration relationship of PVC solution in THF, 30°C.

assumed to exist.⁶ The concentrations from which PVC samples were to be recovered for this work, therefore, were placed well to either side of this "crossover" concentration. Whether or not these aggregation states are carried over into the precipitated solids is a question of relative precipitation and chain relaxation kinetics. In principle, of course, at precipitation the polymer chain conformation and aggregation state should correspond to the dictates of θ conditions.⁷ The rapid addition of nonsolvent, however, will limit the ability of polymer chains to follow the changing thermodynamic conditions imposed by their environment. Thus, we suggest that the entanglement states and chain conformation in the initial solutions will in fact be carried over into the polymer solids.

Mechanical Properties

A summary of stress-strain curve parameters is given in Table I. Reported are values of initial modulus (E_1) at various draw rates, elongation at the yield stress (ϵ_y), and the ultimate elongation (ϵ_R) and stress (σ_R) of the specimens.

As may be expected, the ultimate properties of PVC compounds deteriorate significantly when the polymer has been recovered from solution. The apparent cause is suggested to be a reduction in the polymer entanglement density; were the polymer more highly "plasticized" by undetected amounts of residual solvent, the effect would be in the opposite direction. The influence of initial polymer concentration in solution, though slight, is discernible in ϵ_R and σ_R ; apparently the distinct aggregation states suggested by the solution viscosities (Fig. 1) carry over into the morphology of the resulting solids, as proposed. The effect of drawing rate, pronounced in the control sample, is much reduced in solution-modified versions of the compound. This again appears to be consistent with the assumed morphological changes created by the solution recovery procedure.

TABLE I
Summary of Stress-Strain Parameters^a

Sample	Draw rate cm · min ⁻¹	E_1 (MPa)	ϵ_y (%)	ϵ_R (%)	σ_R (MPa)
Control	0.5	1960	3.7	66	40.5
	2.0	2050	4.1	61	41.5
	5.0	1800	4.2	54	43.8
	20.0	2170	5.5	47	31.2
Soln Mod 0.2%	0.5	2060	2.4	21	29.6
	2.0	2220	2.9	22	30.1
	5.0	2300	2.7	24	29.9
	20.0	2220	2.7	26	29.9
Soln Mod 1.7%	0.5	1850	3.0	27	43.3
	2.0	1970	3.2	29	35.5
	5.0	2140	3.4	32	36.4
	20.0	2100	3.7	34	31.9

^a Experimental reproducibilities: $E_1 \pm 5\%$, $\epsilon_y \pm 0.3$ of stated datum, $\epsilon_R \pm 8\%$ of stated datum, and $\sigma_R \pm 5\%$.

The behavior of these compounds at low deformation differs somewhat from that of polyethylenes,^{2,3} where substantial increases in tensile modulus were produced by disentanglement procedures. In the earlier case, we suggested that in solids formed with polymers recovered from thermodynamically good solvents, chains were in close-packed extended conformations. In the case of the less flexible PVC chain, similar conformational effects may not be discernible by these experimental means.

If the effects of network modification on stress-strain parameters in PVC are less pronounced than corresponding effects in polyethylenes, the response of dynamic mechanical properties amply justifies our concern for establishing relationships linking polymer aggregation states with property balances. The matter is illustrated in Figure 2, showing storage (G') and loss (G'') moduli for the various compounds. The G' decreases systematically, the values for compounds based on PVC recovered from 1.7% THF solutions being roughly midway between the moduli for compounds using PVC as received and as recovered from 0.2% solutions, in which more complete chain disentanglement is assumed. The G'' are even more sensitive to solution treatments, displaying both downward shifts in peak temperatures and peak broadening. Peak broadening may be interpreted as analogous to the effects of dispersing interacting particles in a polymer matrix⁸; the "particles" in this case would be individual chains or chain aggregates dispersed in residual entanglement domains of the matrix polymers.

The influence of solution history on the apparent glass transition characteristics of the PVC compounds, implied by G'' , is more clearly shown by the loss tangent ($\tan \delta$) parameter, in Figure 3, and by initial thermal scans of the compounds, shown in Figure 4. These procedures place the apparent T_g of the compound using PVC without solution treatment at 82°C and 78°C (Figs. 3 and 4, respectively). In solids using solution treated PVCs the T_g

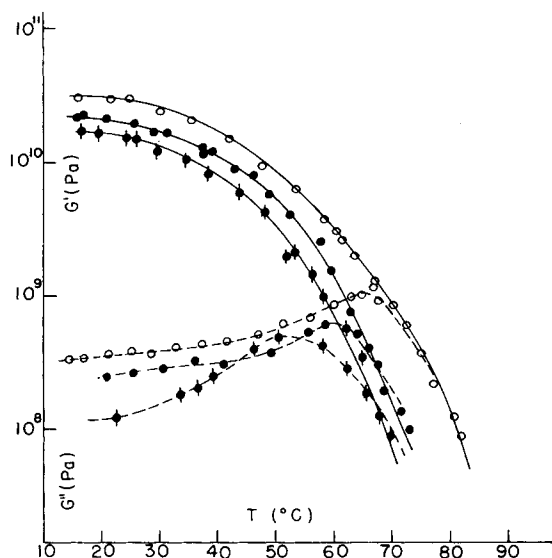


Fig. 2. Response of G' and G'' for PVC compound to solution modification of polymer: (○) control; (●) PVC recovered from 1.7% solution; (●) PVC recovered from 0.2% solution.

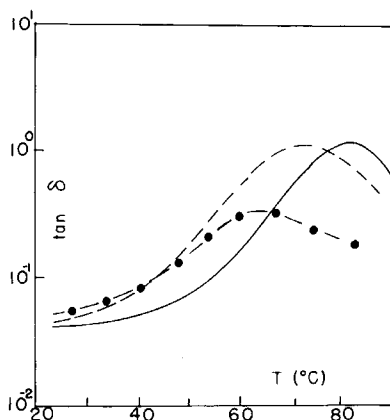


Fig. 3. Loss tangent-temperature relationship for PVC compound: (—) control; (---) polymer recovered from 1.7% solution; (-●-) polymer recovered from 0.2% solution.

reduces to 71°C and 67°C (1.7% solution) and to 66°C and 62°C (0.2% solution). The agreement between results obtained by DSC and dynamic mechanical experiments is good. Since, as already noted, we can exclude any significant presence of solvent residues, the reported T_g decreases are most reasonably due to increases in the free volumes in solids made from solution-modified PVC. An alternative and conceptually equivalent cause would be a more uniform (and rapid) dispersion of plasticizer in polymers recovered from solutions. This latter hypothesis, however, can be rejected because it would call for a time-dependent decrease in the T_g of the *control* polymer, as equivalent homogeneity was attained. As noted below, this consequence is not borne out experimentally.

Time Dependence of Mechanical Properties

The experimental evidence, above, indicates that numerous of the solid-state properties in plasticized PVC depend on the precise state of chain entanglement in the polymer at the time of property evaluation. As a consequence, not all of the measured properties can be equilibrium values, and it is a logical part of the present study to seek information on the rates of equilibrium attainment in polymer compounds where entanglement states had been deliberately altered.

The data summary in Table II confirms the slow, time-dependent shift in mechanical properties, in this case as driven by isothermal annealing at 60°C. The pattern of results is similar to that reported earlier for polyethylenes with modified entanglement states.^{2,3} Particularly noted is the prop-

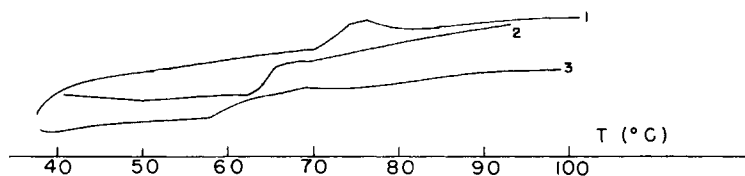


Fig. 4. Initial heating scan of PVC compounds. DSC-2 operated at $5^{\circ}\text{C} \cdot \text{min}^{-1}$: (1) control; (2) polymer recovered from 1.7% solution; (3) polymer recovered from 0.2% solution.

TABLE II
Annealing Response at 60°C of Property Parameters

Property	In. modulus ^a (MPa) (±6%)	ϵ_R (%) (±7%)	T_g (°C) from tan δ (±1.5°)
Control polymer anneal time (h)			
0	2050	61	82
1	2130	62	81
10	2200	70	83
24	2260	77	84
72	2290	76	84
100	2290	81	84
1.7% Soln anneal time (h)			
0	1970	27	71
1	2000	30	73
10	1980	31	74
24	2060	42	76
72	2100	50	78
100	2130	54	79
0.2% Soln anneal time (h)			
0	2060	21	66
1	2110	22	67
10	2070	27	68
24	2100	30	72
72	2130	35	75
100	2180	39	76

^a From data at 2.0 cm · min⁻¹ draw; result is average of five determinations.

erty change in the "control" compounds. Clearly, the morphological state here is not at an equilibrium, but rather reflects the specific effects of the shear/temperature conditions used in sample preparation. Mechanical properties therefore alter as the equilibrium entanglement state is approached, but neither the rate of change nor the sensitivity to entanglement states is common to the property parameters. Thus, for example, initial modulus increases by some 15% from first measurement to the equilibrium datum following some 72 h annealing. The apparent T_g attains constancy after about 24–36 h annealing, but the ultimate properties, as illustrated by ϵ_R —far the most sensitive to entanglement morphology—do not reach equilibrium within the 100 h limit of the present experiments.

In the solution-modified versions, which are in entanglement states far removed from the equilibrium of high entanglement density,⁹ none of the mechanical properties can attain constancy during the 60°C annealing procedure. At these temperatures estimated exposure periods of about 500 h would be needed to approach property equilibria.

The storage moduli of these compounds behave similarly, as illustrated in Figure 5 by G' (at 30°C), and its response to 60°C annealing. The initial linearity of data for the control compound is followed for about 30 h. Thereupon, G' becomes constant, indicating attainment of an equilibrium state. In compounds using the 1.7% and 0.2% solution-modified polymers, the

initial linearity is followed for the duration of the experiment. Periods of about 300 and 700 h would be needed for these compounds to attain the steady-state G' value displayed by the control. The abscissa in Figure 5 ($t^{1/2}$) was chosen on the basis that the kinetics of entanglement-state modification would follow diffusion-controlled processes. The excellent linearity of data in Figure 5 is consistent with this assumption. Extending the argument further, an activation energy should be associated with the process, according to

$$K = A \exp(-E/RT) \quad (2)$$

where K is the isothermal rate constant for equilibrium attainment in any given property of the polymer.

The data in Figure 6 test the hypothesis successfully, by plotting the slope of G' vs. $t^{1/2}$ against $1/T$ (K), and indicate that the activation energy for the process of entanglement modification is about $4.0 \pm 0.3 \text{ kcal} \cdot \text{mol}^{-1}$. This value, of course, is restricted to the present plasticized composition. Reasonably, the rates of entanglement-state modification should vary directly with the degree of plasticization, and a dependence on polymer molecular weight and on plasticizer-polymer thermodynamic interaction can also be anticipated.

Melt Processability

Macromolecular relaxation times are highly temperature-dependent, and it is therefore necessary to show whether or not the processing behavior of plasticized PVC compounds also responds to previous shear, thermal, or solution episodes. In the case of polyethylenes, particularly with molecular

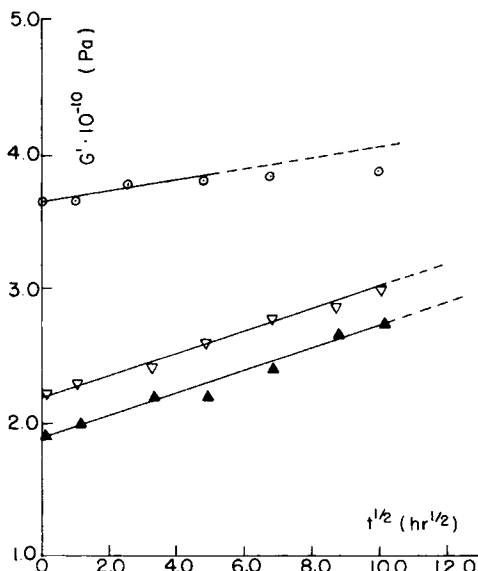


Fig. 5. Time dependent variation of G' . Isothermal annealing at 60°C : (○) control; (∇) 1.7%-solution-modified polymer; (▲) 0.2%-solution-modified polymer.

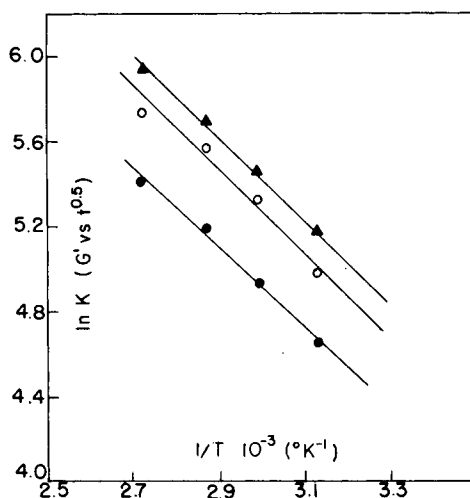


Fig. 6. Arrhenius plot for effect of temperature on the time-dependent variation of storage modulus in: (●) control; (○) 1.7%-solution-modified polymer; (▲) 0.2%-solution-modified polymer.

weight distributions of $M_w/M_n > 5$, the dependence of melt viscosity and melt elasticity parameters on transient states of entanglement coupling frequently has been reported.^{2,3,10} The much narrower molecular weight distributions in PVC polymers, however, could reduce that dependence below the detection level of standard melt processing parameters.

Indeed, determinations of apparent melt viscosity at 190°C, using the gas-driven capillary melt rheometer, failed to show measurable differences among the three compounds involved in this work. (This, incidentally, is a further confirmation that the solution-treatment and compounding procedures did not produce chemical or mechanical degradation, melt viscosities being very sensitive to such occurrences. The absence of bubbling and of voids in the extrudate also lent additional confidence on the absence of solvent traces in the appropriate compounds). An elaboration of responses in the processing of rigid PVC and other plasticized versions of the polymer to entanglement modifications brought about by application of intensive shear will be reported elsewhere. The melt elasticity of the present materials, however, does respond to the state of chain aggregation at the time of testing. This is documented by extrudate swelling data (*B*), in Figure 7. A systematic decrease in *B* is observed at given shear stress, in going from control PVC to compounds using the solution modified polymers. The slope of the *B* vs. $\log P$ relationships also decreases for solution-modified samples, suggesting that the rate of storing elastic energy is reduced by the solution modification process.

Finally, Figure 8 shows the time-dependent change in melt elasticity parameters. These data were obtained by applying pressure to the melt continuously, and sampling the extrudate at 5-min intervals. In this testing mode, the control compound requires a flow time of 15–20 min to attain a steady-state response. In the solution-modified polymers, the amount of change in elastic properties is clearly dependent on the polymer concentration in solution, and steady states have not been reached during the 30

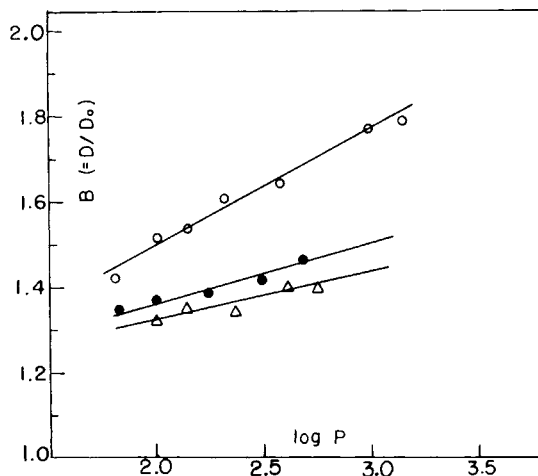


Fig. 7. Swelling ratio vs. extrusion pressure; extrusion at 190°C: (○) control polymer; (●) 1.7%-solution-modified polymer; (△) 0.2%-solution-modified polymer.

min experimental time. Unfortunately, flow times could not be extended beyond this point because of apparatus limitations, nor was it practical to work at lower applied pressures, where reduced B values resulted in a considerable loss of experimental reliability.

One may conclude from these fragmentary results that at least melt elasticity in plasticized PVC compounds is also a function of entanglement state. Thus, such industrially important characteristics as melt strength, edgewise, etc., may be subject to controlled variation in given compounds by the design of appropriate approaches to chain entanglement modification. These same approaches will also influence the bulk of mechanical properties—ranging from apparent T_g , through dynamic mechanical responses, as demonstrated. Finally, the present results again illustrate the contention, first proposed in studies involving fractionated polyethylenes,⁴

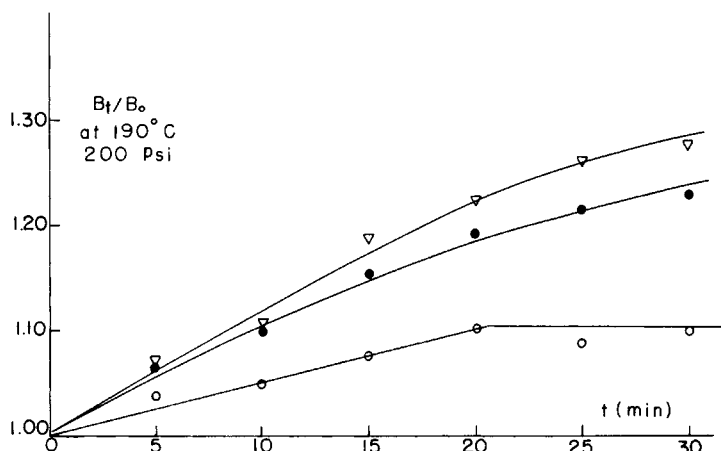


Fig. 8. Illustrating rate process of attaining steady-state swelling; capillary extrusion (190°C) of PVC compounds: (○) control polymer; (●) 1.7%-solution-modified polymer; (▽) 0.2%-solution-modified polymer.

that polymer melt viscosity and melt elasticity respond to different ranges or distances of molecular interactions. The melt elasticity seems linked principally with entanglement density and the existence of long-range coupling leading to deformable network structures. On the other hand, previous⁴ as well as present results point to a closer dependence in melt viscosity on interactions over much shorter distances, possibly on segmental slippage factors. These would be more strongly dependent on the chemistry and the conformation of the chain molecule than on couplings which lead to domain or network morphologies.

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