

# Solution-Induced Changes in the Properties of Polyethylenes

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## Synopsis

The chain entanglement states in high density, linear low density, and low density polyethylenes (HDPE, LLDPE, and LDPE) have been modified by recovering the polymers from solutions in trichlorobenzene (TCB) and *p*-xylene. In the thermodynamically good solvent, TCB, the entanglement density is assumed to be sharply reduced, a condition which is carried over to the corresponding solids. These display transient, but large increments in tensile moduli, slight changes in stress at rupture, and decreases in dynamic mechanical parameters and in elongation at rupture. Scanning calorimetry also shows these solids to have reduced crystallinity. Much smaller property modifications are noted in corresponding samples recovered from *p*-xylene. This liquid is a poorer solvent, particularly for HDPE and LLDPE. The results indicate that property modifications due to deliberate changes in the entanglement states of the polymers are a general phenomenon in the polyethylenes, and the magnitude of property changes depends on parameters of the molecular weight distribution. Chain branching does not seem to be a leading factor in the sensitivity of properties to modifications in the entanglement states. The property modifications produced by the present solution treatments are viewed as guides to the magnitude and duration of shear refining effects to be expected in HDPE, LLDPE, and LDPE polymers.

## INTRODUCTION

The processing behavior and mechanical properties of polymers depend on the morphological state of the material at the moment of testing. Since, in general, relaxation times in high-molecular weight polymers can exceed the time needed for testing, flow and solid-state properties can often be reported when the polymers are in nonequilibrium states. A major contributor to the long relaxation times of polymers is the attenuated response of entanglement couplings to changes in entanglement density caused by the procedures of testing and of processing themselves. Naturally, the magnitude of these effects depends in the inherent capability of polymers to form entanglement networks: flexible macromolecules typified by the polyethylene family are more obviously influenced by previous processing histories than more rigid chain molecules such as polystyrene. Nevertheless, all polymers should be to some degree susceptible to procedures of property modification, as produced by shear refining and, more radically, by solution treatment. Considerable attention has been devoted recently to the effects

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on properties produced by shear and solution episodes<sup>1-4</sup> and on the causes for these effects.<sup>5</sup> It is now appropriate to establish the magnitude of property variations which may be produced by modifying the entanglement density in given polymers and to indicate the degree to which these variations are general to industrially important polymers.

In this article attention is focused on the three major members of the polyethylene family, namely, high density, linear low density, and low density-versions, henceforth coded HDPE, LLDPE, and LDPE, respectively. The mechanical properties of these polymers were evaluated following recovery from solutions in various solvents at a variety of initial concentrations. Property modification by solution treatment is not a practical procedure, but it was used here because very pronounced degrees of disentanglement can be achieved without the danger of mechanical or chemical degradation.<sup>6</sup> The magnitude of property changes which may be achieved can therefore be indicated, at least to reasonable approximations, by this means. Further, by annealing solution-modified polymer samples, it is possible to evaluate the rates of entanglement network reformation, and so to inform on the duration and significance of time-dependent property variations.

### EXPERIMENTAL

**Materials.** The three PE samples, all commercially available, were characterized as to molecular weights and molecular weight distributions by size exclusion chromatography, using solutions in trichlorobenzene (TCB) at 145°C.<sup>7,8</sup> The data are reported in Table I along with the polymer density and melt flow index. Polymer samples were also characterized following solution modification. No experimentally significant changes in the molecular weight values were observed. Thus, the property variations reported below cannot be caused by mechanical or chemical degradation. This conclusion is in agreement with earlier analysis showing polyethylenes to be mechanically and chemically stable following repeated exposure to more severe extrusion cycles.<sup>9</sup>

**Procedures.** The effects of solution history were studied by preparing polymer solutions in the *p*-xylene at 110°C and in TCB at 145°C. Initial polymer concentrations were 0.2 and 2.0% (W/V). These concentrations were selected following determination of solution viscosity vs. concentration relationships for the three polymers. The 0.2% values fell into the linear segments of the pertinent  $\eta_{sp}/c$  vs.  $c$  functions, while the 2.0% values fell into the nonlinear segments characteristic of polymer concentrations above about 0.9–1.2%. These conditions therefore would place the polymers into

TABLE I  
Polyethylene Sample Properties

Type	Molecular weight averages			Melt index (g/10 min)	Density (g/mL)
	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$		
LDPE	60,400	144,500	372,000	0.80	0.921
LLDPE	46,400	185,300	606,700	1.0	0.920
HDPE	46,000	144,000	406,000	0.25	0.951

various states of entanglement modification. At 145°C, TCB is considered to be a very effective solvent for polyethylenes<sup>7,8</sup>; at low concentrations particularly, a high degree of chain disentanglement may be expected. Less pronounced changes in the entanglement states may be expected at the higher concentration and also in the *p*-xylene solutions, xylene being a thermodynamically poorer solvent for the polymers.

Polymers were precipitated by the rapid addition of nonsolvent. Water was used with *p*-xylene, and *n*-butanol with TCB solutions. In principle, polymer precipitation implies that chain conformation attains the characteristic  $\theta$  condition. It has been shown with other polymers, however,<sup>9</sup> that the chain conformation in solution can be carried over into polymer solids if the solidification process is rapid compared with the relaxation times for conformational changes. Rapid nonsolvent addition was practiced in this case to preserve as much as possible, in the solidified polymers, the chain conformations and the entanglement states of their initial solutions.

Precipitated polymers were filtered, washed with nonsolvent, and then freeze-dried for 12 h under 0.2–0.5 Torr pressure. DSC measurements (Perkin-Elmer DSC-2) were made to ensure that the various liquids were removed quantitatively by this procedure. The DSC was also used to measure the fusion properties of recovered polymers. Flake samples of the solution-modified materials were compression-molded in a metallurgical press and heavy duty steel frame at 100°C and ca. 5,000 psi. These conditions were used to reduce as much as possible network restructuring during sample preparation. Certain of the molded samples were used for initial property evaluations, and others were stored at 60°C in air ovens and removed periodically for testing. Stress-strain curves were used to obtain initial modulus, ultimate stress, and elongation at rupture. Dynamic mechanical

TABLE II  
Summary of Stress-Strain Parameters\*

Sample	Tensile stiffness (kg cm <sup>-2</sup> )	Elongation at break (%)	Stress at break (kg cm <sup>-2</sup> )
LDPE			
Control	980	510	120
2.0% xylene	800	470	150
0.2% xylene	1050	380	105
2.0% TCB	1090	400	110
0.2% TCB	1210	300	100
LLDPE			
Control	1150	670	210
2.0% xylene	1100	420	85
0.2% xylene	1350	400	80
2.0% TCB	1550	380	100
0.2% TCB	1800	310	105
HDPE			
Control	6800	720	210
2.0% xylene	4650	530	160
0.2% xylene	4700	560	170
2.0% TCB	7100	510	150
0.2% TCB	7250	460	150

\* All data are for standard jaw separation of 2 cm · min<sup>-1</sup>.

properties were measured with a Rheovibron Model 200 at 11 Hz. All test samples were tumble-blended with 0.2% (W/W) thiophenol antioxidant to stabilize the polymers against possible thermal degradation.

## RESULTS

**Stress-Strain Parameters.** Tensile test results at a standard jaw-separation rate of  $2 \text{ cm} \cdot \text{min}^{-1}$  are summarized in Table II. The results are averages of five determinations with an error of  $\pm 8\%$ . Repeat measurements of tensile properties were conducted at higher deformation rates with results given in Figures 1–3 for LDPE, LLDPE, and HDPE, respectively. A uniform pattern of results is apparent. Polymers recovered from the thermodynamically good TCB solvent display significant increases in tensile stiffness, decreases in elongation at rupture, and slight decreases in breaking stress. The effects are more pronounced in samples recovered from the more dilute solutions. When recovered from the poorer solvent, xylene, the effects are less pronounced. In the case of HDPE no increases in stiffness are observed, suggesting that this polymer is not truly or fully solvated in xylene under the experimental conditions of this work.

Mechanical properties at higher deformation rates are also strongly affected by the presumed changes in entanglement network structures of the polymers, as produced by these solution treatments. We note particularly that initial tensile modulus increases markedly with drawing rate in the TCB-treated polymers. Recovery from xylene either reduces or, in some cases, reverses this trend. Inspection of the data in Table II and in Figures 1–3 shows that the tensile properties of LLDPE respond more strongly to solution treatment in dilute TCB (the most effective route to chain disentanglement) than do the other polyethylenes.

The apparent transient nature of mechanical property changes produced by preparation history is illustrated in Figure 4 for LDPE and HDPE. The data show variations with isothermal ( $60^\circ\text{C}$ ) annealing for times up to 2 weeks. Time to one-half power is used as the abscissa on the assumption that changes in the measured property occur as a result of diffusion-controlled reentanglement processes.

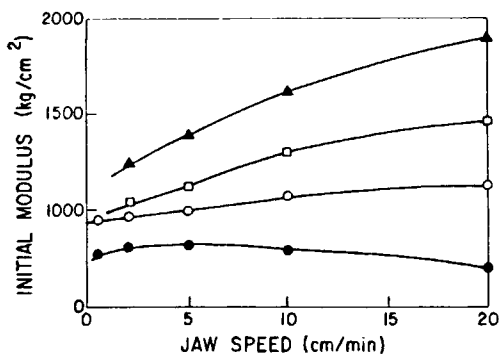


Fig. 1. Initial modulus versus jaw speed, LDPE: (○) control; (●) 2% xylene; (□) 0.2% xylene; (▲) 0.2% TCB.

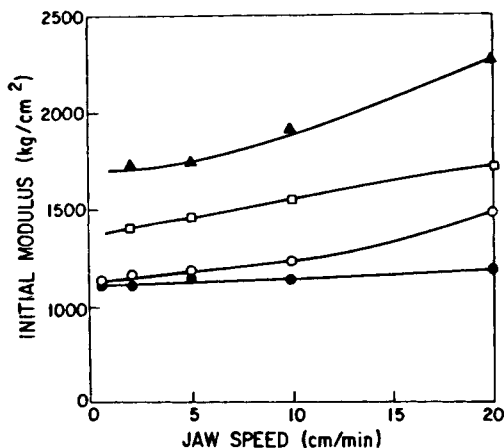


Fig. 2. Initial modulus versus jaw speed, LLDPE: (○) control; (●) 2% xylene; (□) 0.2% xylene; (▲) 0.2% TCB.

An additional overview of results in annealing experiments—involving tensile modulus and elongation at rupture—is given in Table III. This summary is restricted to data for polymers recovered from 0.2% TCB, since this solution appears to produce the most pronounced entanglement reduction in the polymers. Percent changes in modulus and elongation as a function of annealing time were calculated using the corresponding datum for unmodified, control polymer as a comparison value. Noteworthy observations from Figures 4 and Table III are:

(i) The magnitude of property modifications is greatest for LLDPE, and the rate of reversion is slowest for this polymer.

(ii) Property changes in LDPE due to solution treatment somewhat exceed those for HDPE, and the reversion rate is intermediate between LLDPE and HDPE, the reversion rate for the HDPE being the most rapid.

(iii) The HDPE sample appears to be in an equilibrium state of network morphology as received from the supplier (Fig. 4). Slight changes occur in

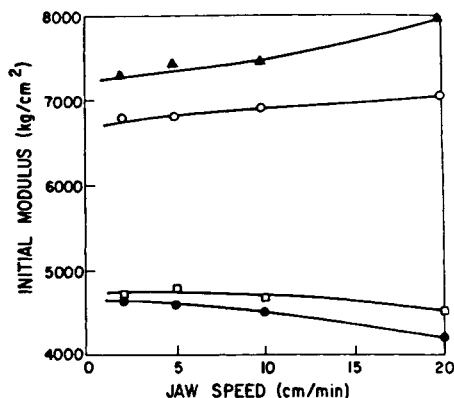


Fig. 3. Initial modulus versus jaw speed, HDPE: (○) control; (●) 2% xylene; (□) 0.2% xylene; (▲) 0.2% TCB.

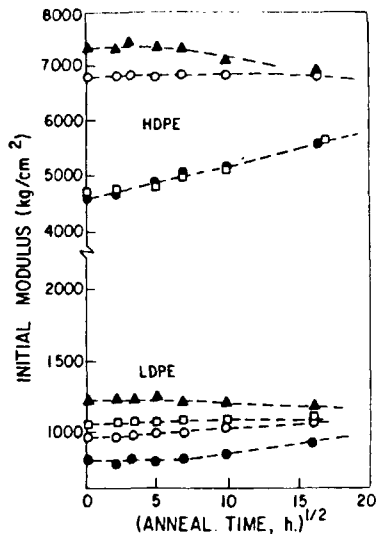


Fig. 4. Response of initial modulus ( $2 \text{ cm} \cdot \text{min}^{-1}$ ) to annealing,  $60^\circ\text{C}$ : (○) control; (●) 2% xylene; (□) 0.2% xylene; (▲) 0.2% TCB.

the properties of control LLDPE and LDPE samples on annealing, suggesting that these materials are not supplied in equilibrium states of network morphology.

**Dynamic Mechanical Tests.** Data were accumulated in the temperature range from  $-140^\circ\text{C}$  to ca.  $40^\circ\text{C}$ . For ease of comparison, parameters were selected from the storage and loss modulus ( $E'$  and  $E''$ , respectively) vs. temperature relationships, and these are given in Table IV. The data show that:

(i) Solution modification of polyethylenes produces major reductions in storage and loss moduli at temperatures below about  $0^\circ\text{C}$  and less significant changes at higher temperatures.

(ii) The magnitude of effects is much greater when TCB solutions are involved and somewhat greater when polymers are recovered from the more dilute solutions. In comparison, at 0.2% and  $110^\circ\text{C}$ , *p*-xylene appears effec-

TABLE III  
Effect of Isothermal Annealing on Mechanical Property Changes Due to Solution Treatment<sup>a</sup>

Polymer	HDPE		LLDPE		LDPE	
	Init. mod.	Elong.	Init. mod.	Elong.	Init. mod.	Elong.
Anneal time (h)	% Property Change <sup>b</sup>					
0	6.7	-28.6	56.5	-53.7	23.5	-41.1
10	5.4	-24.5	52.2	-51.2	21.8	-38.7
24	4.7	-19.1	50.5	-47.9	20.5	-30.0
100	1.5	-13.0	45.6	-39.3	17.9	-27.3
200	0.2	-7.5	38.3	-34.7	11.6	-16.6

<sup>a</sup> Data are for standard jaw-separation of  $\text{cm} \cdot \text{min}^{-1}$ .

<sup>b</sup> % change is calculated from datum on control polymer and corresponding value on sample recovered from 0.2% solution in TCB at  $145^\circ\text{C}$ .

TABLE IV  
Dynamic Mechanical Properties of Polyethylene Recovered from Solution

Polymer	T (°C)	$E'$ (dyn cm <sup>-2</sup> ) × 10 <sup>-9</sup>				$E''$ (dyn cm <sup>-2</sup> ) × 10 <sup>-8</sup>			
		-40	-15	0	20	-40	-15	0	20
<b>LDPE</b>									
Control		41.6	78.0	12.4	5.7	37.5	22.0	12.5	6.3
2.0% xylene		32.2	13.5	11.8	5.5	30.6	19.1	11.7	6.0
0.2% xylene		29.5	18.1	9.4	5.0	28.2	14.4	10.1	5.8
2.0% TBC		30.6	16.3	8.9	5.1	29.5	14.0	10.1	5.6
0.2% TBC		29.2	15.3	8.5	4.7	28.1	13.7	9.2	5.4
<b>LLDPE</b>									
Control		37.5	23.9	12.0	6.2	29.1	19.6	10.9	5.3
2.0% xylene		38.1	22.6	12.2	6.2	28.7	19.2	11.0	5.5
0.2% xylene		34.2	18.8	10.7	6.1	25.2	11.5	9.0	4.6
2.0% TCB		27.1	17.7	10.6	6.0	22.1	13.3	8.8	4.2
0.2% TCB		23.4	16.3	10.0	6.2	20.0	12.4	8.1	4.0
<b>HDPE</b>									
Control		60.3	50.6	41.0	26.6	11.5	9.4	9.4	7.7
2.0% xylene		59.7	51.5	40.3	28.0	11.3	9.6	8.8	7.7
0.2% xylene		55.2	49.6	37.7	24.1	10.4	9.0	8.5	7.0
2.0% TCB		47.0	33.5	28.9	17.4	8.8	7.6	7.6	6.2
0.2% TCB		44.2	30.5	23.5	16.2	8.2	5.8	6.1	5.7

tive in modifying the network morphologies of LDPE and LLDPE, but is ineffective with HDPE. At 2% concentrations in xylene, only LDPE responds to the solvating effect.

**Thermoanalytic Data.** DSC scans were performed on control polymers and on samples recovered from the more dilute solutions in *p*-xylene and TCB. The results of first heating sequences at linear heating rates of 10°C min<sup>-1</sup> are illustrated in Figure 5, while Table V lists values of fusion peak temperatures and of areas under the fusion thermograms. There is a 2–3°C reduction in the fusion peak temperature in polymers recovered from solution and significant reduction in the fusion peak areas. These findings indicate that the overall degree of crystallinity in polymers recovered from solution is decreased, the effects being more pronounced when TCB is the solvent. The reduction in peak temperature also suggests that the crystalline morphology in solution-treated specimens is flawed compared with control samples of the same polymer.

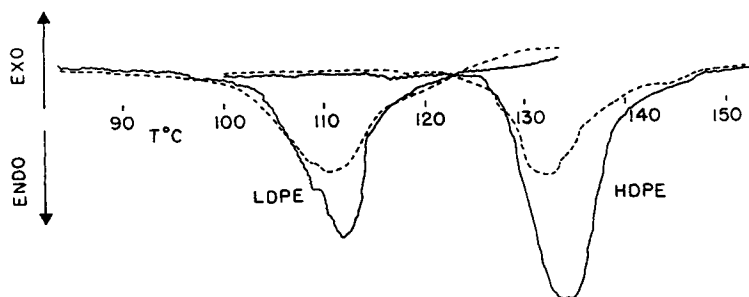


Fig. 5. DSC heating traces (10°C min<sup>-1</sup>): (—) control sample; (---) recovered from 0.2% TCB.

TABLE V  
Parameters of Thermal Analysis in Solution-Modified Polyethylenes

Polymer	Fusion peak temperature (°C)	Area/g sample (arbitrary units)
HDPE control	134	17.4
0.2% xylene	133	15.8
0.2% TCB	131	13.1
LLDPE control	127	15.0
0.2% xylene	126	13.5
0.2% TCB	124	10.6
LDPE control	112	10.3
0.2% xylene	110	9.4
0.2% TCB	110	8.4

## DISCUSSION

The data presented above reconfirm the susceptibility of polyethylenes to property modifications by deliberately produced changes in their entanglement network states. A very broad range of properties is affected, including mechanicals at low and high deformation and the crystalline state of the polymer. As noted elsewhere,<sup>10,11</sup> melt rheological parameters are also influenced, though, of course, the relaxation times in these cases are significantly shorter than is apparent from the persistence of modifications in solid-state properties. Our data make it clear that each of the PE samples studied displays characteristic degrees of solution-induced property modification. The three polymers studied rank in the following descending order of response to modifications in their entanglement network states: LLDPE > LDPE > HDPE. This contradicts a general notion that principally polyolefins with long chain branching are "refinable" (i.e., subject to property modification), by such means as used in this work.<sup>12</sup>

Intuitively, we would expect the susceptibility of polyethylenes to property modification to depend on molecular weight distribution, and particularly on the high moments of the distribution, as given by  $M_z$ . The expectation is based on the concept that the highest molecular weight members of the distribution will exert dominant influences on both the extent and the complexity of entanglement network structures in the polymer, and on the rates of attaining equilibria following network perturbation. Inspection of results in Table I does not entirely substantiate expectations, although the number of samples tested is too small to allow firm conclusions to be reached. The LLDPE sample does follow expectations, however, being the most highly affected by solution treatment in the best solvent medium (0.2% TCB), and also having the highest  $M_z$  value. Further PE samples will be studied in this way to justify more definitive statements about the relationship between molecular weight distribution parameters, the polymer entanglement morphology, and its susceptibility to modification by shear or solution methods.

It is also apparent that the inherent "refinability" of properties in a given



polyethylene cannot be predicted reliably from such standard parameters as the melt flow index. That parameter itself will vary somewhat with the previous processing history of the polymer; furthermore, as seen in Table I, there is no obvious or simple relationship between the melt flow index and any single parameter of the molecular size distribution in the polymer. Thus, in our view, susceptibility to property modification through changes in entanglement states requires the measurement of molecular weights, particularly in the high end of the distribution. This also stresses the need for these high molecular weight fractions to be truly in solution and not merely in swollen, aggregated states.<sup>7,8</sup>

It is interesting to speculate further on the morphology of polymers recovered from solutions. We suggest that in dilute TCB solutions, the polymers are in substantially disentangled states with individual chains in some characteristic extended conformation. Since polymer relaxation times are long compared with solidification times, we assume that these chain characteristics are retained in the solids.<sup>9</sup> The solids evidently develop restricted degrees of crystallinity (Fig. 5 and Table V), and we suggest this to be a major reason for the observed decreases in dynamic mechanical parameters, notably, storage modulus. Surprisingly, however, the tensile moduli invariably increase, in the case of LLDPE by more than 50%. Apparently crystallinity is not the dominant factor in values of this parameter; instead, the property apparently responds strongly to the micromorphology generated by the close packing of randomly oriented chains, which still preserve the conformational state in their solutions.

Solids recovered from *p*-xylene presumably also retain the chain morphology which exists in these solutions. *p*-Xylene, however, is a weak solvent for the polymers. Indeed, as already indicated, it is questionable whether the polymers are in true solutions and not merely in swollen, partly dis-aggregated states. We recall in this respect that Rokudai used *p*-xylene solutions of polyethylenes to counteract the disentanglement effects produced in his work by shear refining.<sup>2</sup> The solids formed from xylene solutions then carry over chain conformations substantially different from those in the TCB case. One reasonable possibility is that the chains are in coiled conformations, and that an appreciable degree of chain entanglement persists. The more loosely packed chains in such solids are assumed to be the cause of tensile property modifications which are very different from those produced in the solids recovered from TCB solutions. Further studies of this type will be required to elaborate on and confirm the mechanisms implicated above.

A final point of interest in our data is the response of tensile moduli to drawing rate (Figs. 1-3). Solids formed from TCB solutions, ostensibly with disentangled chains in close-packed arrays, become stiffer as the deformation rate increases. A possible cause may be the more effective resistance to slippage of chain segments as the period of deformation during the experiment becomes smaller in comparison with the characteristic relaxation time for the slippage process. By the arguments of our hypothesis, chains in the solids recovered from *p*-xylene are in more loosely packed states. Segmental and entanglement slippage on deformation would be expected

to take place more readily in these cases. An inference which can be drawn from these results is that the impact resistance of polymers recovered from TCB solutions will be raised over that of unmodified controls.

The major property effects reported here will, of course, exceed in magnitude the modifications caused by more practical, shear-induced changes in the polymer's entanglement network structure. As will be shown in separate publications, however, the susceptibility of polymers to melt shear refining is in direct relation to the solution-produced effects reported here. By more severely perturbing the network structure, we believe that solution treatments can indicate one limit of property changes to be expected in any given polymer material and thus help design the appropriate melt shear-refining procedure to be applied.

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