

## Effect of Plasticizers on the Viscoelastic Properties of Poly(vinyl Chloride)

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### Synopsis

Stress relaxation modulus data,  $E_r(t)$ , have been determined between  $-70$  and  $+170^\circ\text{C}$  on blends of three samples of poly(vinyl chloride) of different molecular weights with di-2-ethylhexyl adipate, di-2-ethylhexyl phthalate, epoxidized soybean oil, and a poly(propyl adipate), respectively. The relaxation modulus-time-temperature data could be combined into master curves. However, probably owing to the finite contributions of the crystalline phase to the elastic properties, time-temperature superposition is here just marginally valid, and the master curves are only crude, yet still useful approximations. Combination of the present data with the accumulated published information suggests that the viscoelastic properties of plasticized poly(vinyl chloride) are determined primarily by the glass transition temperature of the plasticizer, the compatibility of polymer and plasticizer, and probably also by the crystallites (as cross-links). The exact role of the crystallites will remain elusive until the advent of plasticized poly(vinyl chloride) with controlled crystallinity.

### PURPOSE AND SCOPE

The present study is part of a continuing investigation of the relations between the viscoelastic properties of plasticized poly(vinyl chloride) and the molecular structure of the plasticizers.<sup>1,2</sup> One objective of the work is to clarify the origin of the unusual response of the mechanical properties of poly(vinyl chloride) to plasticization.

The scope of the present work includes the measurement of modulus-temperature-time-concentration relationships for poly(vinyl chloride) blended with several different monomeric and polymeric ester plasticizers. This information is combined with that obtained from earlier work to provide the desired overview of relations between viscoelastic properties of the blend and the molecular structure of the plasticizers.

### EXPERIMENTAL

#### Materials

**Poly(vinyl chloride).** The polymers, products of Union Carbide Corp., and the plasticized samples, kindly supplied by W. R. Grace and Co., were

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characterized by the inherent viscosity in cyclohexanone at 0.2 g/dl. Samples QYSJ, QYSM, and QYSC had inherent viscosities  $\eta_i$  of 0.77, 0.94, and 1.09 dl/g, respectively. No data are available on molecular weight distribution or other sample characteristics.

**Plasticizers.** The physical properties characterizing the plasticizers are presented in Table I. They are of common commercial quality.

TABLE I  
Physical Properties of Plasticizers

Plasticizer		Molecular weight	Density (25°C), g/cc	Dielectric constant (1-100 keps)
Code	Material			
DOA	Di-2-ethylhexyl adipate	370.5	0.927	4.13
DOP	Di-2-ethylhexyl phthalate	390.6	0.986	5.18
EPSO	Epoxidized soybean oil	ca. 1000	0.995	5.47
PE	Poly(propyl adipate) endcapped with fatty acid	ca. 2000	1.07	6.03

**Blends.** All blends contained 2 pph of stabilizer (tin thiol) and 1.5 pph of lubricant (stearic acid) based on poly(vinyl chloride).

### Experimental Techniques

Shear moduli at  $<10^9$  dyne/cm<sup>2</sup> were determined by means of a Gehman torsional stress relaxation balance<sup>3</sup> with a repeatability of  $\pm 8\%$ . Shear moduli at  $>10^9$  dyne/cm<sup>2</sup> [or rather the corresponding shear creep compliance  $J_c(t)$ ] were determined with a Clash-Berg torsional creep apparatus<sup>4</sup> with a repeatability of  $\pm 15\%$ .

Temperature control was obtained as follows. The samples were heated at a rate of 1°C/min in baths appropriate for different temperature regimes: an ethanol bath, a silicon oil bath, and a Tenney environmental test chamber, Model TSU-100. In the latter the sample temperature could be controlled to within  $\pm 0.2^\circ\text{C}$  of nominal temperature.

At higher temperatures, higher heating rates were employed occasionally in order to minimize volatilization of plasticizer.

All samples were cut into rectangular strips  $0.7 \times 0.2 \times 5.0$  cm from pressed sheets and used without annealing. Shear moduli of different sample strips of the same composition were within  $\pm 8\%$  of their average value at any one temperature.

The shear creep compliance  $J_c(t)$  was converted to the shear relaxation modulus  $G_r(t)$  by the relation

$$G_r(t) = \sin m\pi / m\pi J_c(t)$$

where  $m = d \log J_c(t)/d \log t$ . In the data presentation we take  $E_r(t) \approx 3 G_r(t)$ . The shear strain in all experiments has been kept at  $< 10\%$ , in order to retain validity for the approximation of linear viscoelasticity.<sup>5</sup>

## RESULTS

The 10-sec modulus data versus temperature curves were obtained on the thirty-six blends enumerated in Table II. A few typical curves are

TABLE II  
Viscoelastic Parameters from Modulus-Temperature Curves

Plas- ticizer	Parts plas- ticizer	$T_i, ^\circ\text{C}$			$-s$		
		QYSC	QYSM	QYSJ	QYSC	QYSM	QYSJ
DOA	35	8	11	9	0.025	0.028	0.027
	50	-21	-19	-20	0.033	0.033	0.031
	65	-37	-38	-41	0.037	0.036	0.036
DOP	35	21	22	16	0.037	0.039	0.041
	50	-4	-2	-4	0.044	0.043	0.040
	65	-20	-20	-18	0.056	0.054	0.050
EPSO	35	27	27	23	0.046	0.042	0.049
	50	7	6	5	0.050	0.052	0.050
	65	-7	-7	-8	0.059	0.059	0.059
PE	35	27	26	28	0.056	0.050	0.055
	50	12	12	12	0.050	0.050	0.048
	65	1	1	-2	0.054	0.059	0.061

presented on Figure 1 and 2. These curves yield the following characteristic data: The inflection temperature  $T_i = T$  at  $E_r(10) = 10^9$  dyne/cm<sup>2</sup>, and the slope  $s = -d \log E_r(10)/dT$  at  $T = T_i$ , all of which have been assembled on Table II. The effect of polymer molecular weight shown on Figure 2 appears to be the same for all four plasticizers examined, namely, that the modulus of the rubbery phase of resin QYSC is about the equivalent of one plasticizer concentration step (15 pph) above that of the lower

TABLE III  
Viscoelastic Parameters from Master Curves

Plas- ticizer	Parts plas- ticizer	$T_i, ^\circ\text{C}$		$n$		$T_p, ^\circ\text{C}$	
		QYSC	QYSJ	QYSC	QYSJ	QYSC	QYSJ
DOA	35	10	7	0.22	0.23	190	175
	65	-43	-38	0.23	0.22	179	153
DOP	35	15	13	0.30	0.28		
	65	-17	-17	0.31	0.28		
EPSO	35	26	23	0.24	0.27	—	177
	65	-7	-9	0.31	0.29	182	162
PE	35	29	26	0.26	0.27	195	177
	65	-0.5	-2	0.30	0.29	183	163

molecular weight resin QYSJ. The relation of  $T_i$  to plasticizer type and concentration is shown in Figure 3. The lower end of the curves,  $T_i$ , of the plasticizers has not yet been determined.

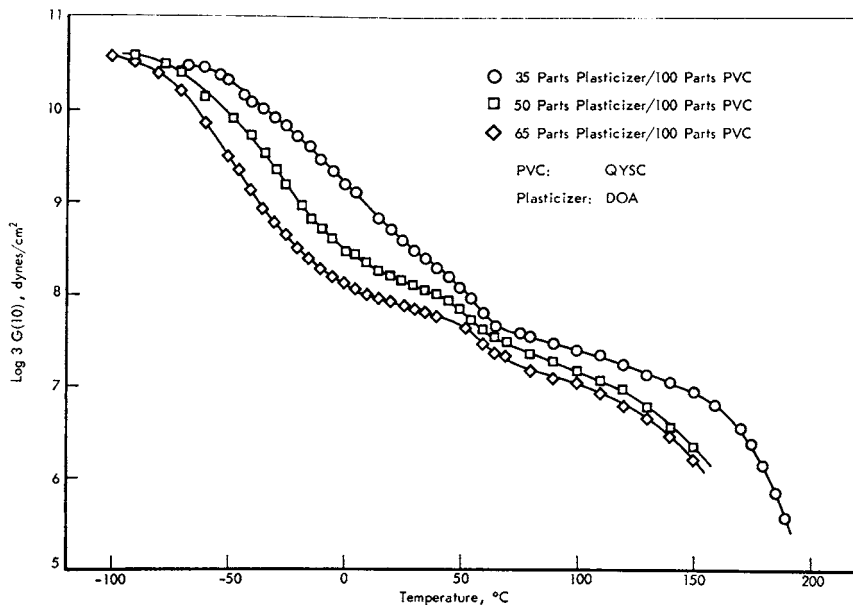


Fig. 1. Modulus-temperature curves for plasticized poly(vinyl chloride).

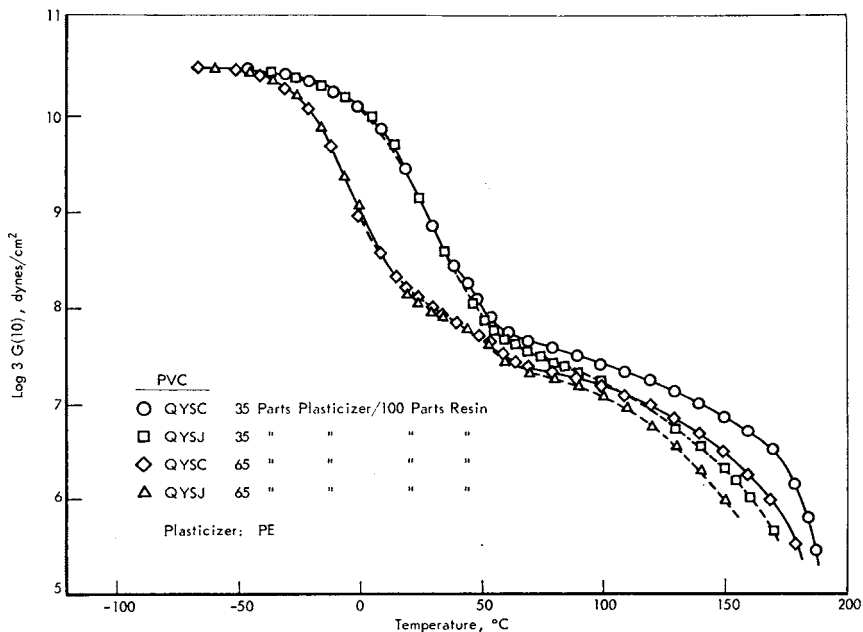


Fig. 2. Modulus-temperature curves for plasticized poly(vinyl chloride).

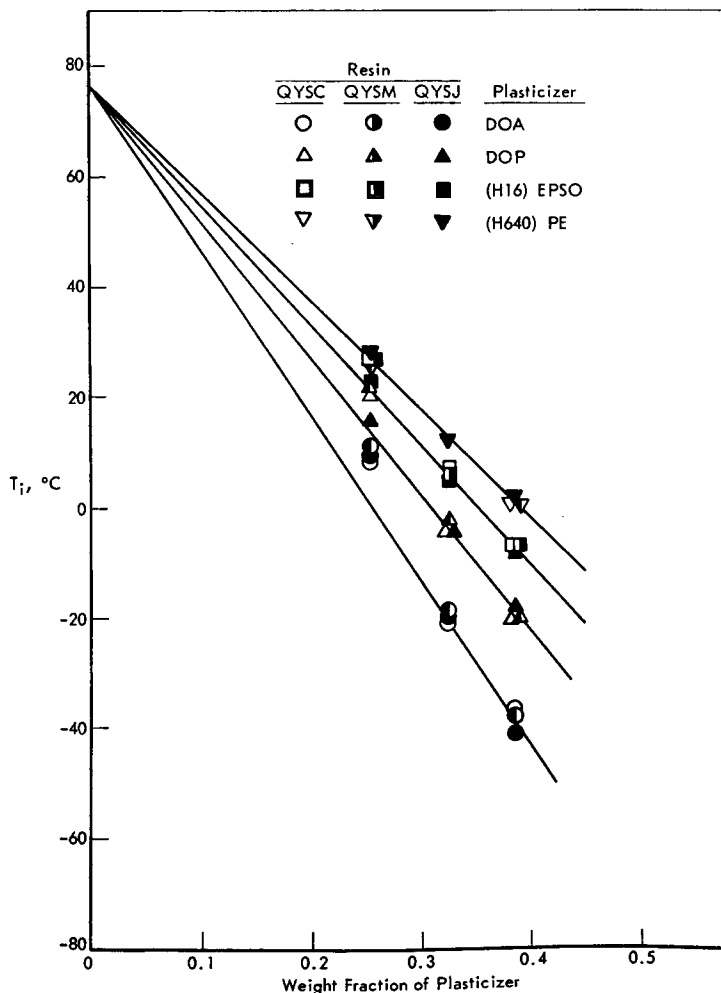


Fig. 3. Inflection temperature vs. weight fraction of plasticizer for plasticized poly(vinyl chloride).

Relaxation modulus versus time data were obtained at several temperatures for the sixteen blends enumerated on Table III. The temperatures were so chosen that the stress-relaxation data covering two to three decades in time, shown on Figure 4, could be combined by horizontal shift (time-temperature superposition) into a continuous viscoelastic master curve (exemplified by Figs. 5 and 6) for each sample. The inflection temperature  $T_i$ , defined earlier, is taken as the reference temperature for each master curve.

In view of the existence of at least one secondary relaxation ( $\beta$ ) process in poly(vinyl chloride) in the temperature range under consideration, as well as its reasonably well established partial crystallinity,<sup>6</sup> one had no reason to

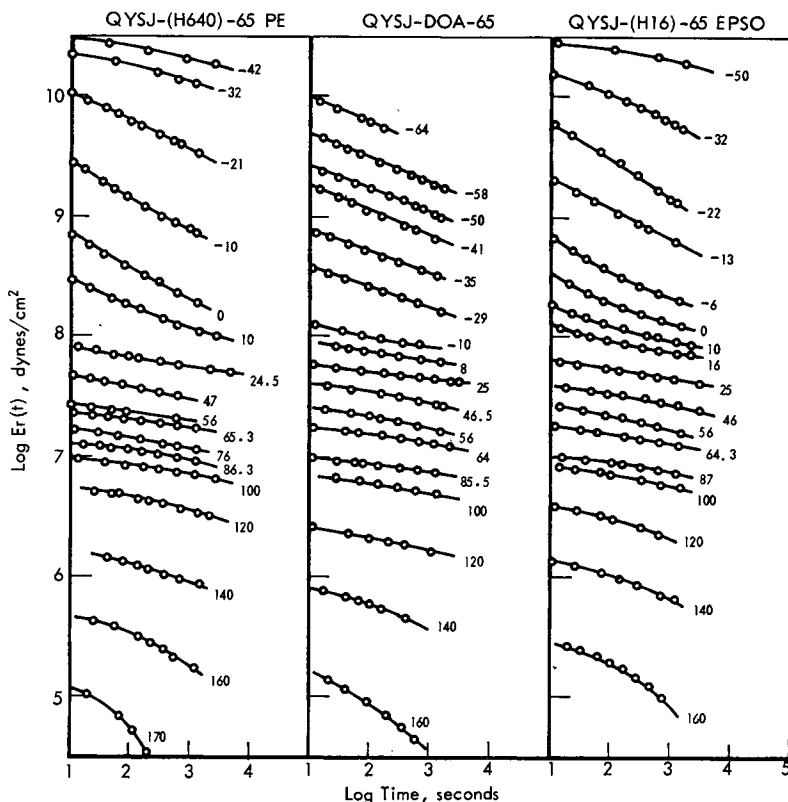


Fig. 4. Modulus-time curves for plasticized poly(vinyl chloride).

expect completely smooth master curves. Indeed, the individual modulus-time curves do not join entirely smoothly. However, within the admittedly narrow framework of the existing data all data points appear to straddle the "master curve" to within  $\pm 0.15$  in  $\log E_r(t)$ . Over most of their range the curves are smoother than that. No effort has been made so far to assess the effect of this vertical uncertainty on the uncertainty in the horizontal shift factor  $K(T)$ . It may be as large as  $\pm 0.2$  in  $\log t$ .

The master curves can be roughly characterized by the inflection temperature  $T_i$ , the slope  $n = -d \log E_r(t)/d \log(t)$ ,  $K(T)$  at  $K(T) = 10$  sec, and the "flow temperature"  $T_f = T$  at  $E_r(t) = 10^5$  dyn/cm<sup>2</sup>. This slope  $n$  must obviously be related to the temperature slope constant  $s$ , such that at  $t = 10$  sec

$$\log E_r(10) = 9 - np(T - T_i)$$

where  $p$  should be a universal constant and  $np = s$ , if the time-temperature superposition principle were truly valid. The data of Table IV show that the identity  $np = s$  is on the whole quite well obeyed, but the nonuniversality of  $p$  clearly indicates that time-temperature superposition is not an entirely valid procedure for plasticized poly(vinyl chloride).

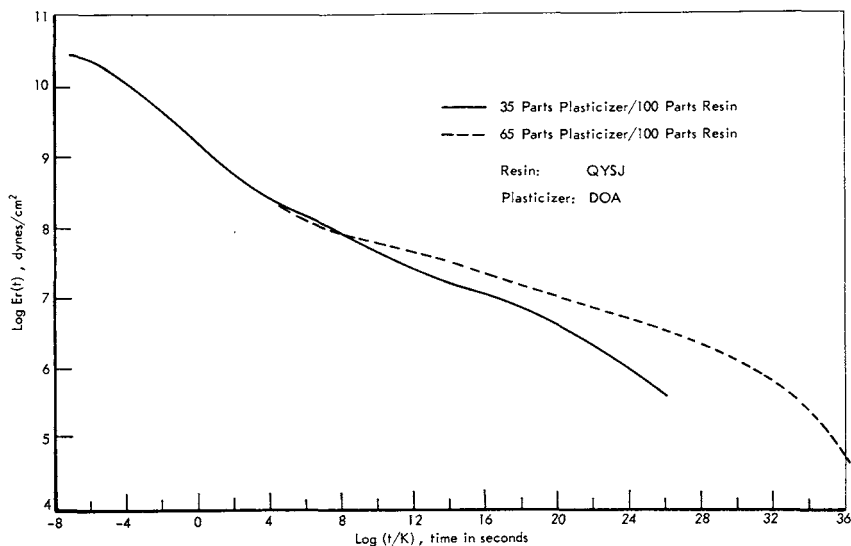


Fig. 5. Master curves for plasticized poly(vinyl chloride).

TABLE IV  
Viscoelastic Parameters from Master Curves

Plasti- cizer	Parts plas- ticizer	$p$		$np(s)$	
		QYSC	QYSJ	QYSC	QYSJ
DOA	35	0.120	0.132	0.026 (0.025)	0.030 (0.027)
	65	0.200	0.173	0.046 (0.037)	0.038 (0.036)
DOP	35				
	65				
EPSO	35	0.165	0.172	0.040 (0.046)	0.046 (0.049)
	65	0.177	0.200	0.055 (0.059)	0.058 (0.059)
PE	35	0.173	0.200	0.045 (0.056)	0.054 (0.055)
	65	0.183	0.213	0.055 (0.054)	0.062 (0.061)

### Effect of Composition

Plasticizers are added to solid polymers primarily in order to depress their glass transition temperature  $T_g$  and therefore shift the modulus-temperature curve to lower temperatures. Specific effects of plasticizer chemistry on the viscoelastic properties of the blend should therefore be readily discernible on a plot of  $\log E_r(10)$  versus  $T/T_g(12)$ , where  $T_g(12)$  is the glass transition temperature of the blend. Typical examples from earlier work are shown on Figures 7 and 8.

Here one finds that butyl phthalate, a rather good solvent for the polymer, hardly changes the shape of the elastic modulus temperature curve. The far less compatible solvent di-2-ethylhexyl succinate, by contrast, drastically changes the shape of the curve at  $T > T_g$  in the direction

toward sharply reduced slope  $s$  and correspondingly raised level of the shear modulus in the leathery and rubbery regime.

The data obtained in the present investigation fit into the pattern of

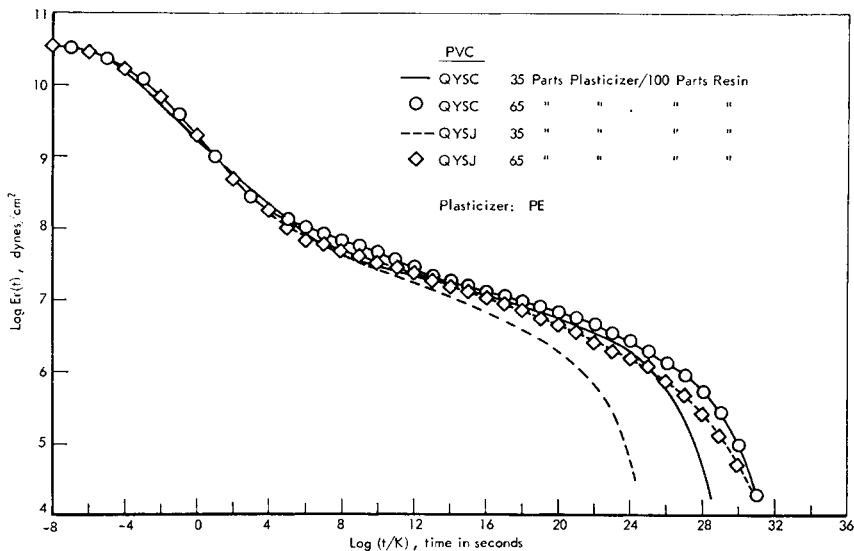


Fig. 6. Master curves for plasticized poly(vinyl chloride).

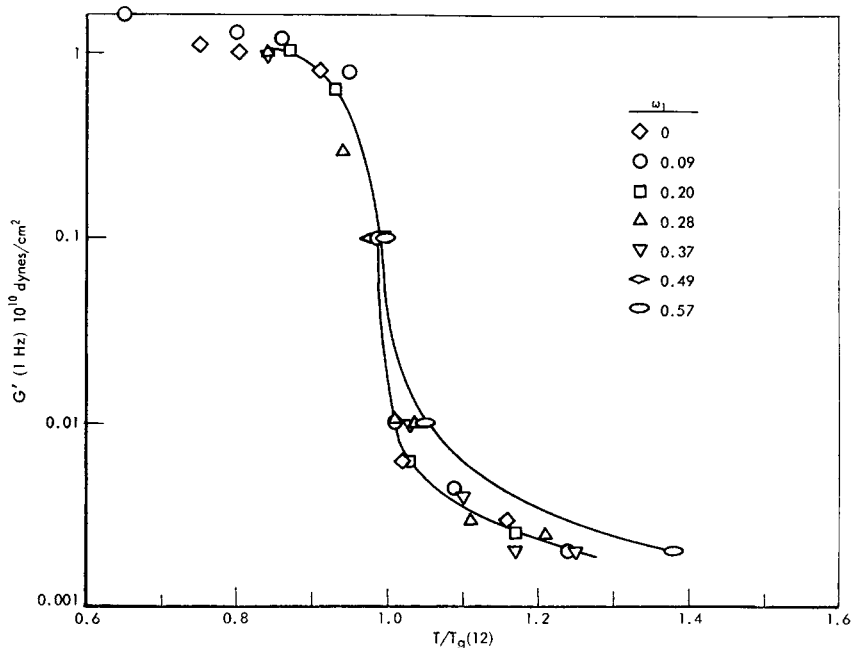


Fig. 7. Shear modulus of poly(vinyl chloride plasticized with varying weight fractions  $w_1$  of dibutyl phthalate vs.  $T/T_g(12)$ .



these two early model experiments. Typical examples are shown on Figures 9 and 10. Where  $T_g$  data have been lacking,  $T_i$  has been used as reference temperature. Since in general  $T_i$  is within  $\pm 5^\circ\text{C}$  of  $T_g$ , this choice should create no major distortion.

The previous graphs do not show very clearly the drop in the slope  $s$  of these curves at  $T = T_i$  which inevitably accompanies the addition of plasticizer to a glassy polymer, albeit to widely varying degree. A plot of  $s$  as function of plasticizer composition and concentration on Figure 11 is all the more interesting.

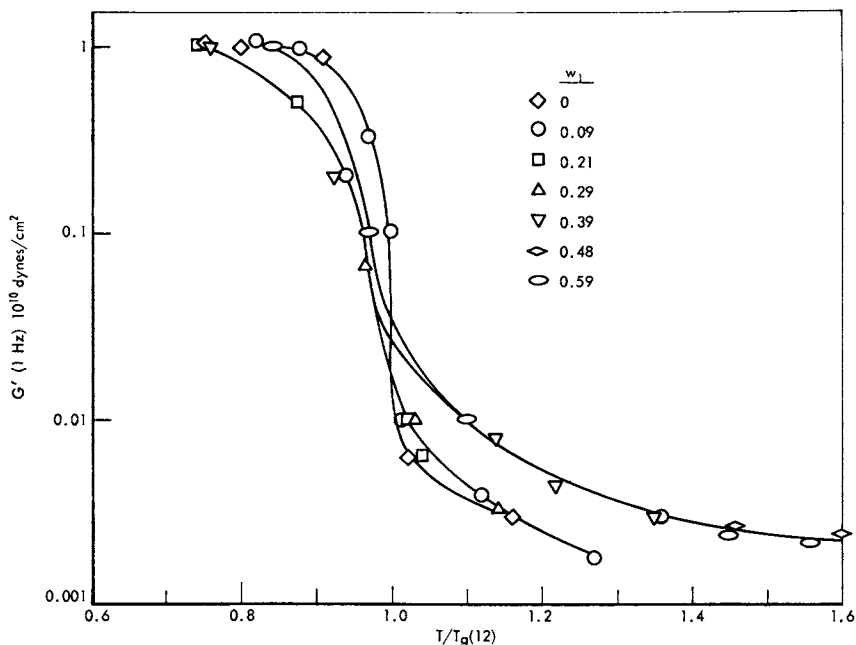


Fig. 8. Shear modulus of poly(vinyl chloride) plasticized with varying weight fractions  $w_1$  of di-2-ethylhexyl succinate vs.  $T/T_g(12)$ .

The peculiar shape of these curves, i.e., their passage through a minimum, points to the relation between this slope and the magnitude of the mechanical energy loss ( $\tan \delta$ ) in dynamic measurements. At the inflection point  $d \ln E_r(t)/d \ln \omega \big|_{T_i} \sim \tan \delta_{\max}$ . Moreover, at that point  $\omega = \omega_{\max}$ , and  $d \ln \omega_{\max}/dT = \Delta E^\ddagger/RT^2$ , where  $\Delta E^\ddagger$  is the activation energy. Hence  $s = -d \ln E_r(10)/dT \big|_{T_i} \sim \Delta E^\ddagger/RT^2 \tan \delta_{\max}$ .

Inspection of the available data relating  $\tan \delta_{\max}$  to plasticizer concentration<sup>7-9</sup> shows that  $\tan \delta_{\max}$  for mechanical energy loss and for dielectric energy loss passes through a minimum at some concentration  $\phi_{\min}$  of plasticizer. The magnitude of  $\phi_{\min}$  differs somewhat between the two types of measurement, but that need not concern us here. The origin of that minimum, however, is quite obvious.

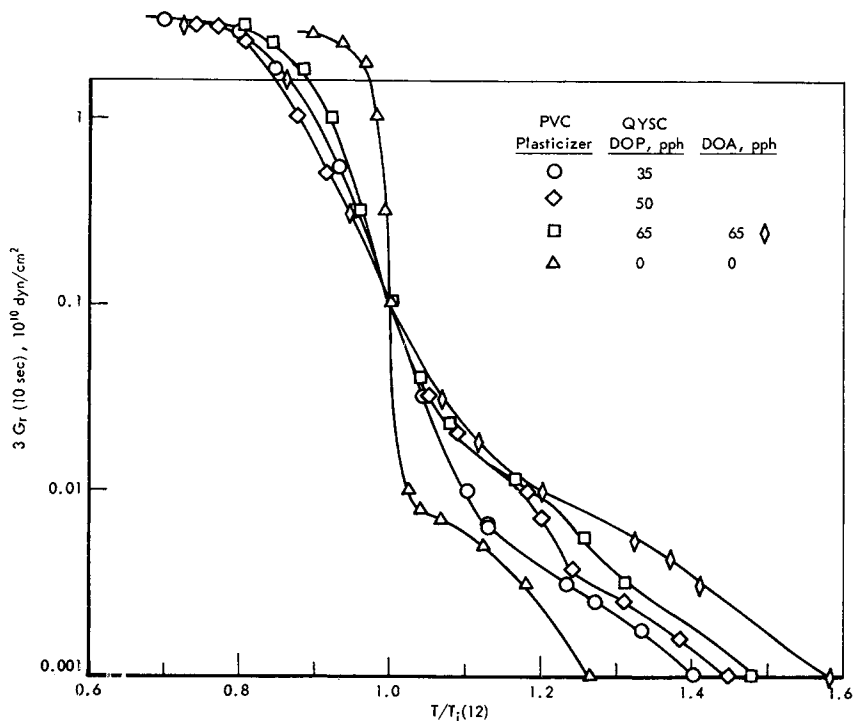


Fig. 9. Relaxation modulus of poly(vinyl chloride) plasticized with dioctyl phthalate and with dioctyl adipate vs.  $T/T_i(12)$ .

One may consider  $\tan \delta_{\max}$  as a measure of the concentration of volume elements in transition. Hence dilution of the polymer by plasticizer reduces the magnitude of  $\tan \delta_{\max}$ . However, at high plasticizer concentration the glass transition temperature of the plasticized polymer enters a temperature region approaching the glass transition temperature [ $T_g(1)$ ] of the plasticizer. Thus the "wings" of the  $\tan \delta$  curve of the plasticizer begin to contribute to  $\tan \delta_{\max}$  of the plasticized polymer and make it rise again (Fig. 12).

The activation energy  $\Delta E^\ddagger(12)$  of the blend should be the (geometric) average of the activation energies of the components (at  $T_i$ ) corrected for the interaction energy,  $F^E$ . Since  $\Delta E^\ddagger(1)$  at  $T_i(1)$  of some plasticizers (especially those composed of cyclic molecules) can be of similar magnitude as  $\Delta E^\ddagger(2)$ , the curve of  $\Delta E^\ddagger(12)$  versus  $\phi$  can pass through a shallow minimum. In the technically important plasticizer concentration range  $T_i$  drops so rapidly with increasing plasticizer concentration that  $\Delta E^\ddagger(12)/RT_i^2$ , while reflecting the magnitude of  $\Delta E^\ddagger(1)$ , is almost invariant over an appreciable concentration range.

The foregoing argument suggests that the trend of the slope constant  $s$  (on Fig. 11) reflects the combination of activation energy  $\Delta E^\ddagger(1)$  and solubility characteristics for the plasticizer-polymer combination. The

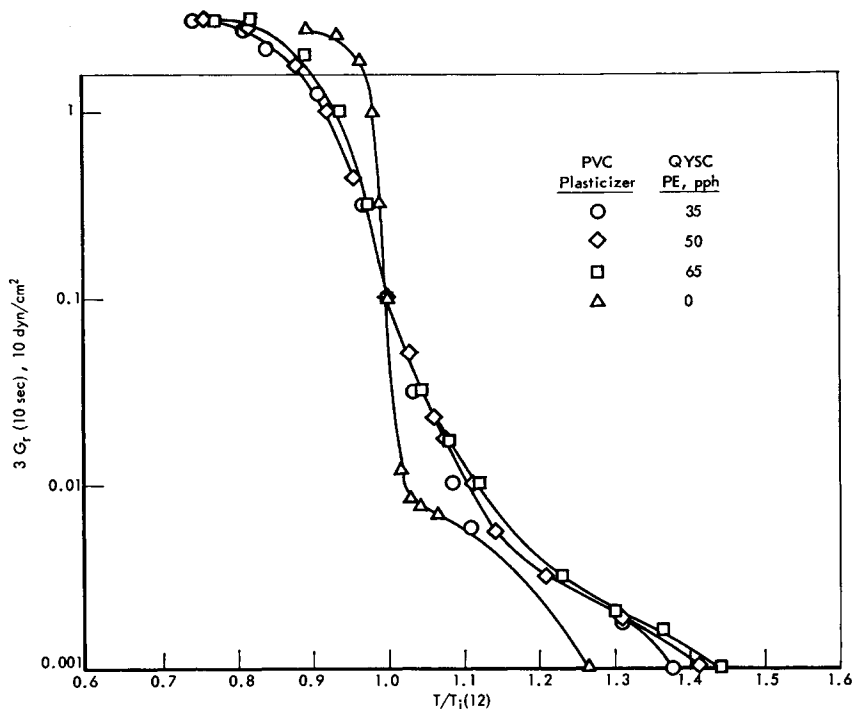


Fig. 10. Relaxation modulus of poly(vinyl chloride) plasticized with poly(propyl adipate) vs.  $T/T_i$  (12).

TABLE V

Plasticizer	$\Delta E^\ddagger$ , <sup>a</sup> kcal/mole	$\mu^b$	$(\delta_2 - \delta_1)^2$ , <sup>c</sup> cal/cm <sup>3</sup>	Reference
Tricresyl phosphate	13.1	0.38	1.0	12
Di-2-ethyl hexyl phthalate	11.3	$0 \pm 0.02$	1.0	2,10
Di- <i>n</i> -butyl phthalate	7.7	-0.05	0.1	11
Poly(propylene adipate)		0.22	0.5	10
Ethoxylated soybean oil				10
Di-2-ethylhexyl succinate	7.0	0.39	1.1	11
Di-2-ethylhexyl adipate	6.0	0.28	1.2	10
Tri-2-ethylhexyl phosphate	6.5	-0.30	2.0	12

<sup>a</sup> See Ref. 11.

<sup>b</sup> Flory solvent-polymer interaction parameter for plasticizer-PVC pairs.<sup>13,14</sup>

<sup>c</sup>  $\delta_1$ ,  $\delta_2$  Hildebrand solubility parameters of blend components 1 and 2.

data in Table V are in good qualitative agreement with that expectation. While a full treatment of this subject will be presented elsewhere, it is worth noting that compatibility, as expressed by the Flory interaction parameter  $\mu$ , is a second-order rather than a first-order effect on the slope constant  $s$  (Table V).

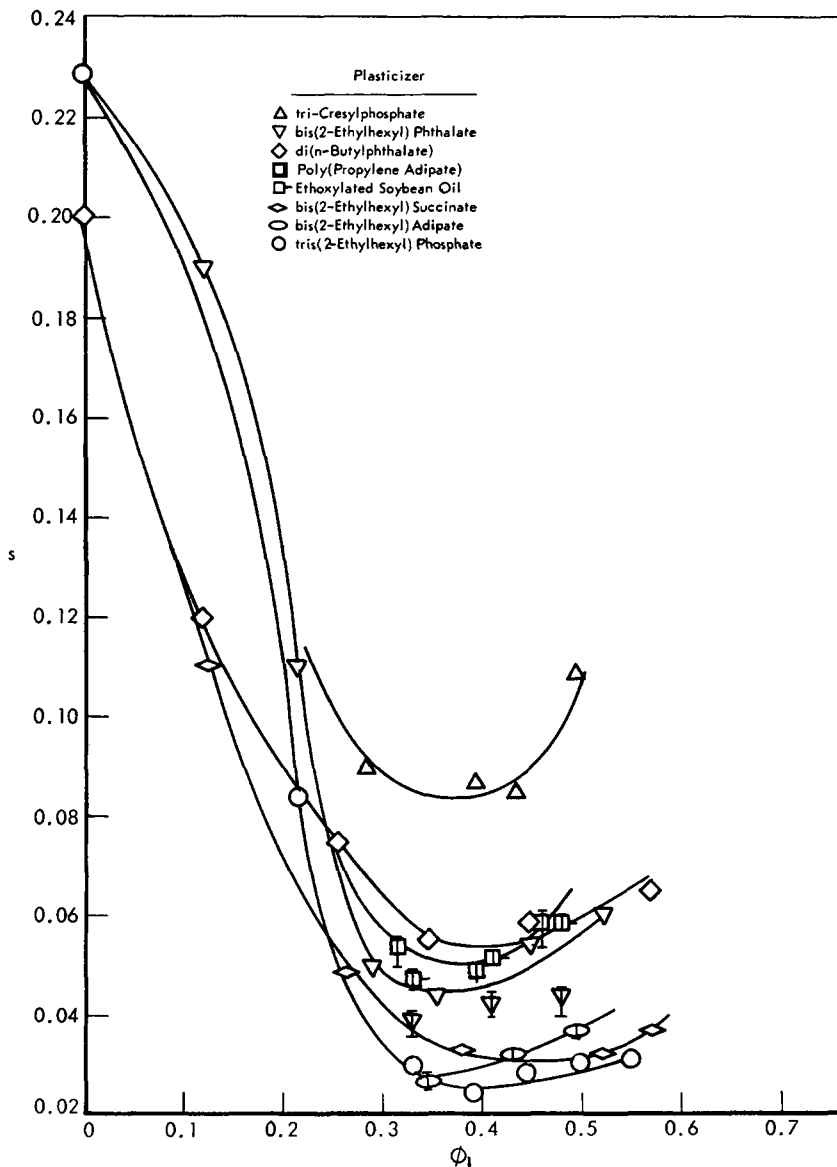


Fig. 11. Temperature slope constants for various plasticizer-PVC blends as function of volume fraction of plasticizer.  $\Delta E$  and related data used to calculate  $s$  are presented in Table V.

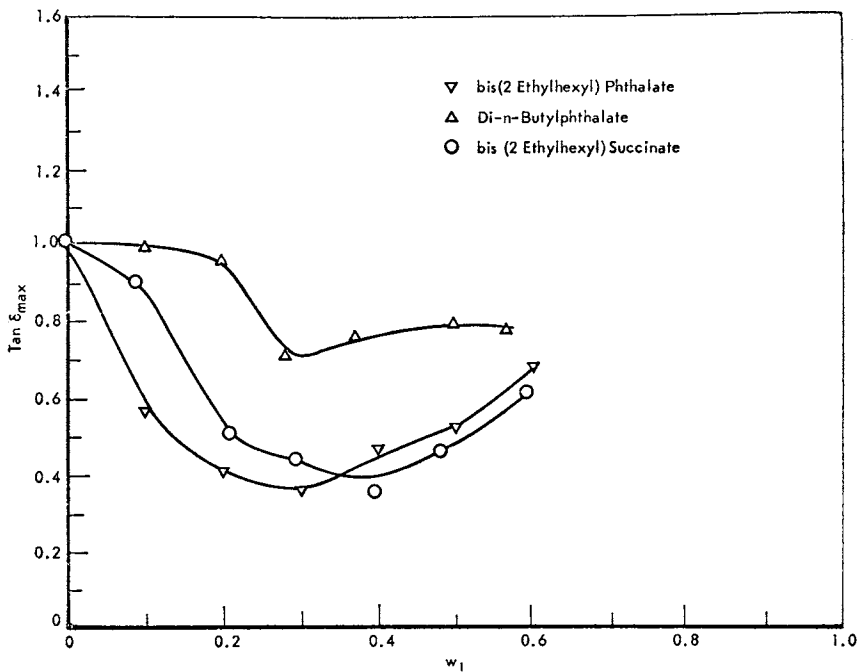


Fig. 12. Envelopes of the height of  $\tan \delta_{max}$  of plasticized poly(vinyl chloride) as a function of weight fraction of plasticizer: ( $\nabla$ ) di-2-ethylhexyl phthalate;<sup>10</sup> ( $\blacktriangle$ ) di-*n*-butyl phthalate;<sup>11</sup> ( $\circ$ ) di-2-ethylhexyl succinate.<sup>11</sup>

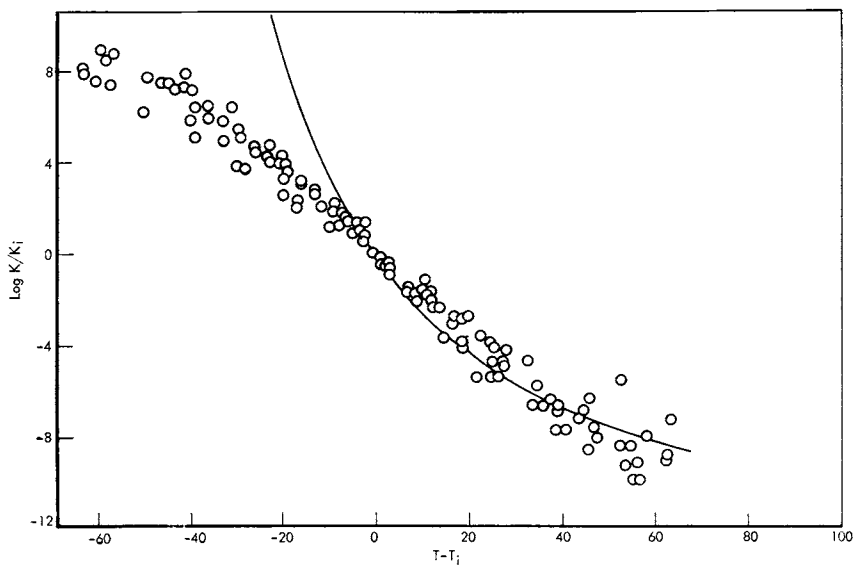


Fig. 13. Plot of temperature dependence of characteristic relaxation times for plasticized poly(vinyl chloride).

Owing to the close coupling between time and temperature and the near identity of  $T_i$  with  $T_g$ , there are no surprises in the composition effects on the master curves, all of which have their respective  $T_i$  as reference temperature. At  $E_r(t) < 10^8$  dyn/cm<sup>2</sup> the modulus level (at a fixed reduced time) rises with increasing plasticizer concentration, as it does on the  $E_r(10)$  versus  $T/T_g(12)$  graphs. Compatibility also has the expected effect of depressing the level of  $E_r(t)$  in the rubbery region.

The near coincidence of the master curves, especially at short times, for the two concentrations shown, is not representative of the general concentration relations but results from the accidental choice of the two concentrations. The earlier experiments with the system dioctyl phthalate-PVC,<sup>2</sup> covering a much wider range of plasticizer concentrations, clearly show a wide fanning out of the master curves at short as well as at long reduced times. The algebraic relation of curve-shape to plasticizer concentration has yet to be developed.

The representation of the temperature dependence of the shift factor  $K(T)$ , the relative relaxation time of the system, as  $\log K(T)$  versus  $T - T_i$  as well as the dependence of  $K(T)$  on a very high power of the polymer concentration are well known from the work of Ferry<sup>15</sup> as well as others. It is very gratifying to find again that the relaxation time at  $T$  relative to that at  $T_i$ , namely,  $K(T)/K(T_i)$  is a function of the difference  $T - T_i$  only, as shown in Figure 13, and is essentially independent of plasticizer composition and concentration. This observation suggests that the relative relaxation time of a plasticized system is largely determined by the magnitude of  $T_g(12)$ .

The location of the WLF viscosity temperature curve on Figure 13 suggests that a different relation is needed to represent the data far below  $T_g$  or  $T_i$ .

### Effects of Polymer Crystallinity

The exceptionally useful range of mechanical properties of highly plasticized poly(vinyl chloride) has long been ascribed to the crosslinking effect of its few but uniformly distributed crystallites. This concept was generated by the observation of the complete recovery of extensive deformation of the rubbery phase,<sup>16</sup> pointing to the existence of permanent crosslinks in the amorphous molecular network. The absence of chemical crosslinks—evident from the free flow of the melt—combined with the x-ray diffraction and the stress optical evidence for the presence of crystalline domains of poly(vinyl chloride) obtained by Tobolsky et al.<sup>6,17</sup> then suggested that widely distributed small crystallites of the "fringed micelle" type act as crosslinks for the amorphous network.

The recent work by Sabia and Eirich<sup>5</sup> established the extent of deformation at which the crystallites too are deformed and permanent set is observed. One of the objectives of the present work was to pinpoint the evidence of crystallinity obtained from viscoelasticity at small strains. Such evidence might have been produced had it been possible to work at

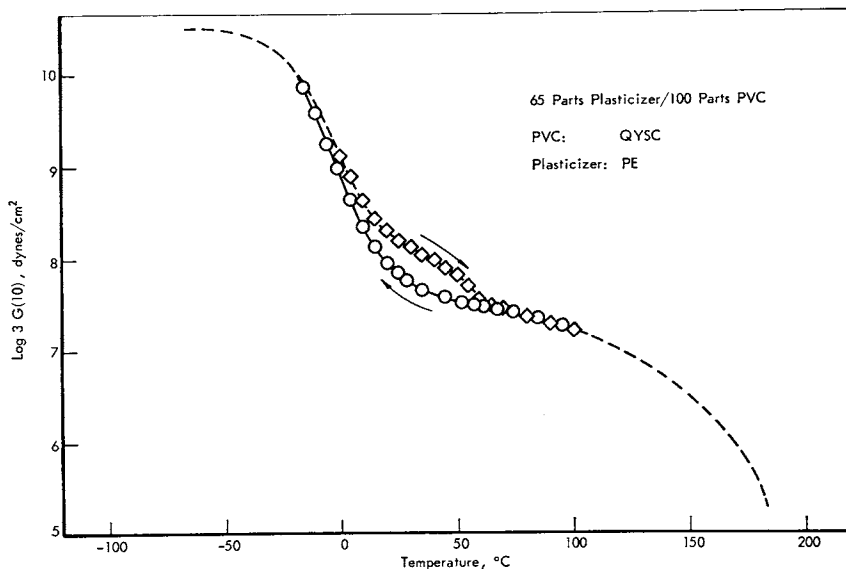


Fig. 14. Modulus-temperature curve for plasticized poly(vinyl chloride).

known and controlled levels of crystallinity. In the absence of such data we shall see that assumed crystallinity can explain some of the observations, but that experiments done at small strains yield only vague clues regarding the relation between viscoelastic properties and crystallinity.

The steady decrease of the relaxation modulus of plasticized PVC with increasing temperature in the rubbery regime, shown on Figures 1 and 2, is more like that of a simple glassy polymer than like that of a crosslinked rubber. The relaxation modulus of the latter is either independent of temperature between  $1.05 T_g$  and  $T_F$ , or may even rise with increasing temperature in that region, as demanded by the kinetic theory of rubber elasticity.<sup>3</sup> The negative temperature coefficient of  $E_r(t)$  may either be due to interaction energy contributions, as considered in nonideal rubber elasticity, or to the successive melting of crystallites at less than bulk melting temperature because of their size distribution into near molecular dimensions, a familiar phenomenon with semicrystalline polymers.

The comparatively high level of the flow temperature  $T_F$  has been ascribed to the melting of crystallites, but noncrystalline polymers of sufficiently high degree of entanglement can also exhibit such high values of  $T_F$ . Hence, the dependence of  $T_F$  on molecular weight and on plasticizer concentration, exhibited by the data of Table III, does not provide adequate support for the postulated crystallinity.

A more striking point is the strange bump at about 50°C in the modulus-temperature curves of Figures 1 and 2, the location of which on the temperature scale seems to be independent of plasticizer composition and concentration. This facet could also point to secondary relaxation process discontinuities. However, its disappearance upon reheating and rapid

cooling of the sample, as shown by the lower curve of Figure 14, points to a phenomenon associated with a separate, possibly a crystalline phase.

## CONCLUSIONS

The primary effect of plasticizers is to lower the glass transition temperature of the polymer and therefore to shift the inflection point of the elastic modulus versus temperature curve, and with it the entire curve, to lower temperatures. The extent of this reduction depends largely on the glass transition temperature of the plasticizer.<sup>18,19</sup>

The temperature dependence and the level of the elastic modulus of the plasticized blend at  $T > T_g$ , one measure of its technological usefulness, appears to be governed by the nature of the polymer, by the viscosity-temperature function of the plasticizer, and by the somewhat vaguely defined "solvency" of the plasticizer for the polymer.

Partial crystallinity is still considered to be the primary cause of the significantly higher elastic moduli of plasticized poly(vinyl chloride) than of plasticized purely glassy polymers. Yet the present viscoelastic measurements made at small strains, while consistent with such a picture, cannot be used as independent evidence for its correctness. There is a real need for experiments with plasticized systems with controlled degrees of crystallinity.

The degree of crystallinity prevailing in the present samples of PVC was sufficiently small that it interfered in an observable but only minor way with the construction of master curves by time-temperature superposition of the stress relaxation curves.

Within the error range of the superposition procedure the magnitude of the relative relaxation time  $K(T)/K(T_i)$ , calculated from the shift factors (from the construction of the master curves) is given by a single curve of  $\log K(T)/K(T_i)$  versus  $T - T_i$ , irrespective of plasticizer type and concentration.

Thus it appears that plasticizers affect the viscoelastic properties of the blend primarily by determining the level of the glass transition temperature and secondarily, if still very importantly, through solvent-solute interaction with the polymers.

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