

The Effect of Plasticizing Compounds on Acrylic Fibers

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Synopsis

Comparison of the various solubility parameters of different plasticizing agents has shown that their plasticizing action on Acrilan filaments is governed by polar interactions. The diameter swelling of the filaments appears to decrease with increasing efficiency of the plasticizing agent. The diffusion of a disperse dye through the plasticized fiber is not related to the fiber swelling and is controlled by the plasticizing action of the dyebath.

INTRODUCTION

Previous work has shown that the reduction in the glass transition temperature (T_g) which occurs when Acrilan filaments are immersed in aqueous solutions of plasticizing agents is responsible for the observed improvement in dyeing properties.¹ It is generally assumed that enhanced dyeing properties are a result of fiber swelling in the dyebath. If this is so, a connection between plasticization and swelling can be expected.

The majority of plasticizing compounds examined in search of such a correlation caused a reduction in the T_g and an increase in the diameter swelling of the Acrilan filaments. The effect is not universal, however, and compounds have been found which cause a slight increase in the T_g and in the swelling, while others cause marked swelling with very little change in T_g . Under certain conditions, a slight contraction in the fiber diameter can accompany a reduction in the glass transition temperature.²

Work was therefore undertaken to examine the effect of plasticizing agents on acrylic fibers more closely; this work is reported here.

EXPERIMENTAL

The experimental work involved measurements of (a) the glass transition temperature of Acrilan fibers in various aqueous solutions of plasticizers; (b) the diameter swelling of the fibers; (c) the partition coefficient of the plasticizing compounds between the fibers and water; and (d) the diffusion coefficient of C.I. Disperse Orange 3 into plasticized fibers.

Determination of the Glass Transition Temperature (T_g)

The experimental procedure was the same as described in a previous publication.¹ Bright Acrilan 3 denier filaments (supplied by Monsanto) were pretreated in a tensionless state in the appropriate liquid. A light load was attached to a long monofilament and immersed in an appropriate solution of plasticizing agent. The length of the filament was carefully recorded at different temperatures. A marked discontinuity at the glass transition temperature was observed when the filament length was plotted against temperature.

Determination of the Swelling of Acrilan Filaments

The change in diameter of the filaments was taken as a measure of the degree of swelling. The procedure for determining this change was as follows:

Chopped filaments (0.1 g) were pretreated for 24 hr in closed quickfit tubes containing appropriate solutions (100 ml) at 95°C. The fibers were filtered from the solution, mounted on a microscope slide, and their diameter measured microscopically while still wet. One hundred measurements were made for each treatment and the mean value taken.

The increased swelling was expressed as a percentage change relative to the swelling in water, i.e.,

$$\frac{D_p - D_w}{D_w} \times 100\% = \text{percentage diameter swelling}$$

where D_p and D_w are the mean diameters of the fibers treated in the plasticizer solution and in water, respectively.

The results of the measurements of swelling and T_g are summarized in Table I. The effects range from a marked decrease to a small increase in the T_g , some compounds having little if any effect on the T_g . All the additives caused some swelling, but there is no correlation between the magnitude of the swelling and the change in the T_g . In particular, the addition of water to benzyl alcohol causes a detectable reduction in the diameter swelling.

Determination of the Partition Coefficient of Various Plasticizing Compounds Between Water and Acrilan

Conclusions drawn from the effects of equimolar solutions of different plasticizing agents are open to doubt because each agent has a different partition coefficient. Consequently, the results represent the effects of different concentrations of carrier in the fiber.

Partition coefficients of each plasticizing agent were therefore determined at 75° and 95°C. The results were used to determine the concentration of plasticizer in the fiber, and this in turn facilitated a comparison of the effects of equimolecular concentrations of the plasticizers in the fiber.

A weighed sample of fiber (1 g) was equilibrated for 2 hr in a solution (50 ml) of the appropriate concentration of plasticizing agent and the concentration of plasticizer determined before and after equilibration, using a spectrophotometer. The results are summarized in Table II.

TABLE I
Glass Transition Temperature and % Diameter Swelling of Acrilan Filaments
in the Presence of Water and Different Organic Compounds at Various Concentrations

Effect on T_g	Medium	Compound	Initial concentration of compound in solution, C_{S_0} , mole/l.	T_g , °C	Diameter swelling, %
Decrease	water	—	—	57.0	0 (reference sample)
	water	<i>n</i> -amyl amine	0.10	51.0	81.38 (Fibers became tacky)
			0.20	46.0	
			0.30	40.5	
	water	<i>n</i> -amyl alcohol	0.05	55.0	7.41
			0.10	54.0	9.98
			0.15	53.5	10.26
	benzyl alcohol	—	—	59.0	5.50
	benzyl alcohol	water	0.56	55.0	5.41
			1.00	—	4.57
			1.11	52.0	4.38
			1.67	48.0	4.57
			2.00	—	2.99
			2.22	44.5	2.52
			3.00	—	1.87
Unchanged	water	1,5-diaminopentane	0.10	58.5	56.34
			0.20	58.5	60.30
			0.30	58.5	69.16
			0.40	—	75.40
	water	glycerol	0.10	59.0	9.23
			0.20	58.5	11.14
Increase	water	diethylene glycol	0.30	58.5	12.12
			0.10	61.0	9.65
			0.20	61.5	11.61
	water	1,5-pentanediol	0.30	61.5	11.84
			0.10	60.0	9.88
			0.20	60.0	11.33
	water	1,2-diaminoethane	0.30	60.0	10.49
			0.10	61.0	13.20
			0.20	62.0	20.90
			0.30	62.5	24.67
	water	Ethanediol	0.40	62.0	25.19
			0.10	62.0	6.81
0.20			62.5	6.92	
0.30			63.0	6.95	
air	—	—	0.40	64.0	6.76
			—	90.0	0.19

The values in Table II were used to calculate the concentration of plasticizer in the fibers immersed in solutions covering a range of concentrations. The standard heat of adsorption for each plasticizer was calculated in the usual manner, and the results are also tabulated. They show that absorption of the plasticizing agent is exothermic.

TABLE II
Variation of the Partition Coefficient of Plasticizers Between Water
and Acrilan, with Temperature

Plasticizer	Temperature, °C	Partition coefficient	Standard heat of absorption ΔH , kcal/mole
2-Ethylphenol	75	15.03	-3.69
	95	11.25	
<i>m</i> -Cresol	75	11.93	-1.38
	95	10.71	
Aniline	75	8.93	-0.38
	95	8.67	
<i>o</i> -Ethylaniline	75	27.25	-1.89
	95	23.50	
<i>m</i> -Toluidine	75	11.64	-0.97
	95	10.79	
Benzylamine	75	2.65	-3.09
	95	2.08	
Benzyl alcohol	70	2.37	
	95	1.87	

Measurement of Diffusion Coefficient of C.I. Disperse Orange 3 into Acrilan Filaments

The procedure adopted was identical to that described elsewhere.¹

Solubility Parameters

If the Hildebrand and Scatchard^{3,4} equation is valid for the case of plasticizers in Acrilan, the maximum efficiency of plasticization will be expected when the solubility parameter (δ) of the plasticizer and Acrilan coincide. However, the value of the solubility parameter for polymers or liquids may contain contributions from both polar forces and dispersion forces. Consequently, when considering interactions between molecules, it is important to know the relative importance of the different types of intermolecular forces involved. Various approaches to this problem have been reviewed.^{5,6} When hydrogen bonding is absent, the solubility parameter may be split into polar and nonpolar components.⁷ Various workers have also formulated solubility parameter components which account for the effects of dispersion, dipole-dipole, induction, and hydrogen-bonding forces.^{5,8,9}

In the present work, the solubility parameters were split into two components only, the dispersion component and the association component. The latter represents the contribution of all intermolecular forces, other than dispersion forces, to the value of the solubility parameter.

Values for the total solubility parameters where available, were taken from Hansen⁸; when they were unavailable, the heat of vaporization was determined from the boiling point of the liquid, using the empirical Hildebrand Rule,⁴ and the solubility parameter was calculated in the usual way. The values of total solubility parameter were then split into the two components, using the homomorph concept⁷ and eq. (1),

$$\delta^2 = \delta_d^2 + \delta_a^2 \quad (1)$$

where δ is the total solubility parameter, δ_d is the dispersion component, and δ_a is the association component.

The solubility parameters of the polymer were derived from the corresponding values for the liquid most closely resembling the monomer unit, i.e., propionitrile; δ_d was calculated for the corresponding homomorph using Small's molar attraction constants.¹⁰ It was assumed that the nonpolar and polar contributions to the total cohesive energy density of the monomer remain the same in the polymer. The solubility parameters of the polymer were then calculated from the cohesive energy, the molar volume being calculated from the density of the polymer and the molecular weight of the repeat unit.

The values obtained for polyacrylonitrile were

$$\delta_d = 9.47 \text{ cal}^{0.5}/\text{cm}^{1.5}$$

$$\delta_a = 8.32 \text{ cal}^{0.5}/\text{cm}^{1.5}$$

Literature values of the total solubility parameter for polyacrylonitrile^{10,11} are given as $12.7 \text{ cal}^{0.5}/\text{cm}^{1.5}$ and $15.4 \text{ cal}^{0.5}/\text{cm}^{1.5}$. The value of $12.7 \text{ cal}^{0.5}/\text{cm}^{1.5}$ was taken here.

DISCUSSION

The extent to which a particular solution of plasticizing agent will reduce the T_g of Acrilan filaments will depend upon (a) how much plasticizer is absorbed by the fiber (i.e., the partition coefficient), and (b) the chemical structure of the plasticizing molecule. If the plasticizer operates entirely by increasing the free volume of the polymer system, the efficiency of the different plasticizer molecules will depend only upon their free volume, and a linear relation will be obtained between the volume fraction of plasticizer in the polymer and the reduction in T_g . This is the picture when only dispersion forces are operative but it is to be expected that the situation will be more complicated with the plasticizing molecules and the highly polar acrylic fibers used in this investigation.

The differences in efficiency between the various compounds examined is represented by the slopes of the lines in Figure 1, where a comparison is made of the reduction in the T_g of Acrilan filaments caused by equimolar concentrations of plasticizing agents in the fiber. Similar linear relationships are obtained when comparing the effects of equal volume fractions of plasticizer in the fiber.

When the compounds are placed in order of magnitude for their effect on the T_g , some of the compounds take up different positions in the list, depending upon whether the comparison is being made for the effect of equal volume fractions or equal molar concentrations in the fiber (Table III). This does not appear to be of major importance in the context of this paper, however, because the change in position is due to a variation of no more than 4°C in the T_g . What are significant are the large differences in the effect on T_g caused by different compounds, which indicate that properties other than the volume fraction are important in the plasticizing process.

The action of plasticizing agents on textile fibers has already received

much attention in relation to the "carrier dyeing" of polyester fibers, and many reviews are available. Attempts have also been made to correlate the various properties, such as solubility parameters, dielectric constants, and di-

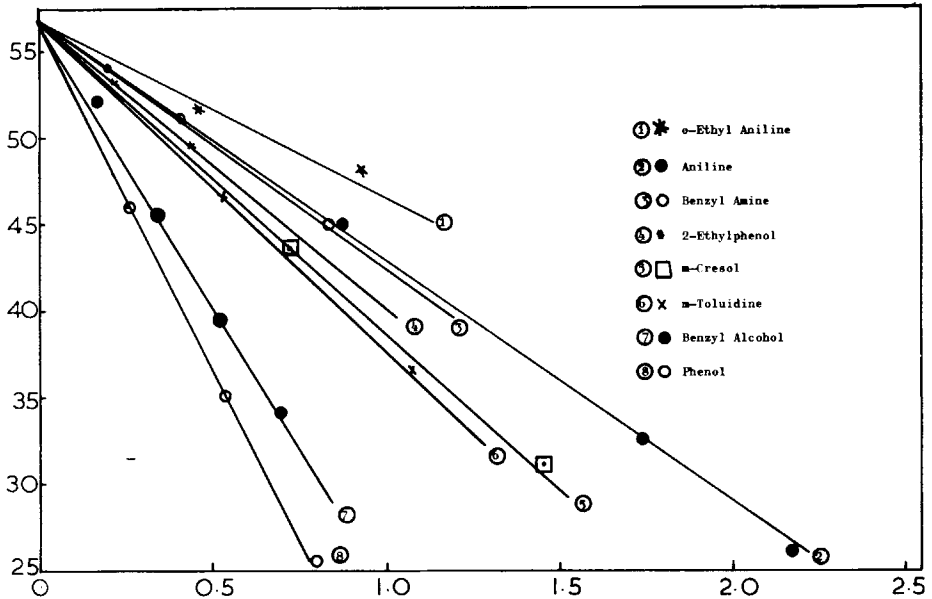


Fig. 1. Effect of plasticizer content on the T_g of Acrilan filaments: ordinate, T_g ($^{\circ}\text{C}$); abscissa, plasticizer content of filaments (mole per kg of dry filament).

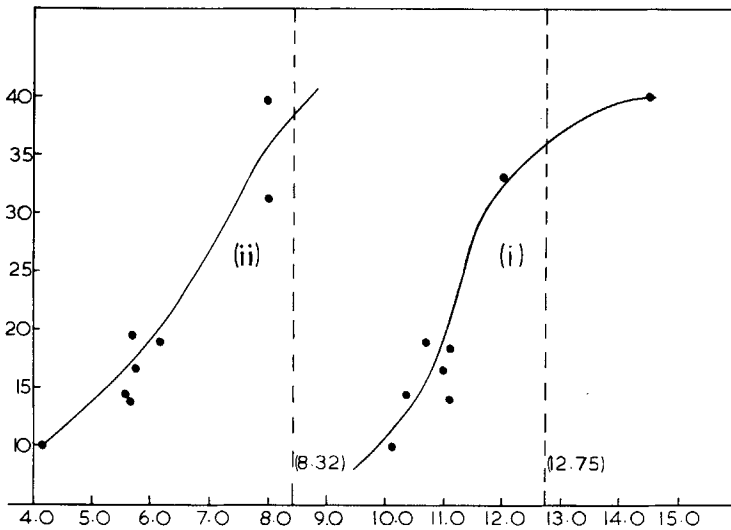


Fig. 2. Reduction in T_g (ΔT_g) caused by equimolecular concentration of plasticizer in Acrilan filaments related to (i) total solubility parameter δ ; (ii) association solubility parameter δ_a : ordinate, plasticizing effect ΔT_g ($^{\circ}\text{C}$); abscissa, solubility parameter ($\text{cal}^{0.5}/\text{cm}^{1.5}$). Broken vertical lines represent the total solubility parameter (12.7 $\text{cal}^{0.5}/\text{cm}^{1.5}$) and the association solubility parameter (8.32 $\text{cal}^{0.5}/\text{cm}^{1.5}$) for polyacrylonitrile.

TABLE III
Order of Plasticizing Efficiency of Some Amino and Hydroxy Compounds

Plasticizer	Reduction in T_g , ° C, of Acrilan filaments with respect to their T_g in Water, caused by		Plasticizer
	1 mole plasticizer/ kg fiber	$10 \cdot 10^{-2}$ volume fraction of plasticizer in fiber	
Phenol	40.0	41.3	phenol
Benzyl alcohol	33.0	30.5	benzyl alcohol
<i>m</i> -Toluidine	19.2	19.2	<i>m</i> -cresol
<i>m</i> -Cresol	18.2	18.5	<i>m</i> -toluidine
2-Ethylphenol	16.6	17.5	aniline
Benzylamine	14.4	16.4	2-ethylphenol
Aniline	14.0	12.0	benzylamine
<i>o</i> -ethylaniline	10.2	11.1	<i>o</i> -ethylaniline

pole moments of the plasticizing molecules, with their activity on acrylic fibers.¹² Although the dipole moment appeared to provide some indication of their plasticizing efficiency, there is very little general correlation between any one property and the plasticizing action.

Other studies concerning the plasticization of polyester fibers made comparisons of the effects of equal molecular concentrations in the solution surrounding the fiber, but it is the concentration of the plasticizing agent within the fiber which is relevant, because the action takes place within the fiber.

Comparison of the Solubility Parameters of Plasticizing Agents and Polymer

The solubility parameter is often taken as a guide to the ease of mixing of a solvent and a polymer. In the present investigation, the effects of equal molecular concentration of the plasticizer in the Acrilan fibers were correlated with the solubility parameters of the plasticizing agents. This correlation produced the results shown in Figure 2, where the reduction in T_g (ΔT_g) caused by the plasticizer is plotted against both δ and δ_d . No correlation was found between ΔT_g and δ_d . The maximum plasticizing efficiency occurs when the association solubility parameter of the fiber and plasticizer coincide, and therefore polar forces must play a dominant role in the plasticization process.

It should, however, be pointed out that the effects observed are the combined effects of water and plasticizing agent. A full explanation of the facts must take into account the competition which exists for the polar sites between the polar water molecules and the molecules of the plasticizing agents. Correlations with the properties of the plasticizing agent in an aqueous system are presumably possible because the amount of water in the hydrophobic fiber is small and does not vary greatly with changes in the concentration of the plasticizing agent. Consequently, its effect will be constant over the range of concentrations of plasticizing agent used.

Corresponding graphs are given for the relationship between the diameter

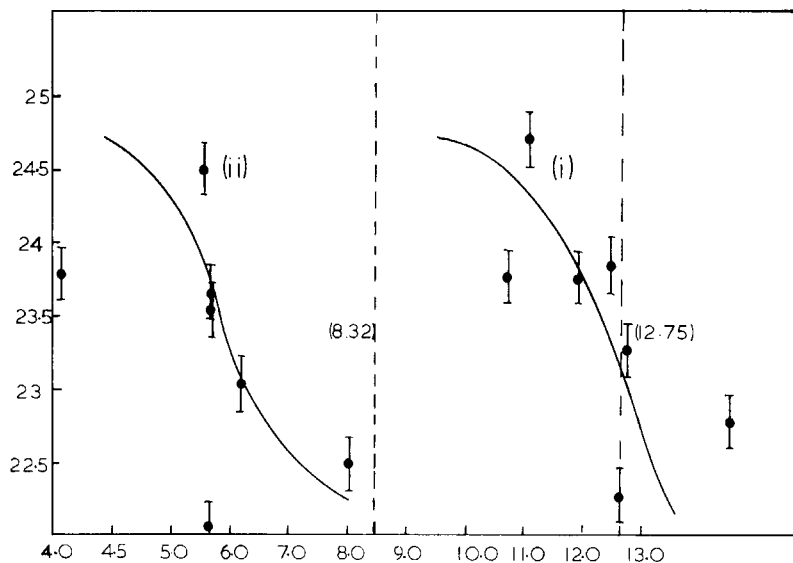


Fig. 3. Diameter of Acrilan filaments containing 1 mole/kg of plasticizers, related to (i) the total solubility parameter of the plasticizer δ ; (ii) the association solubility parameter δ_a : ordinate; diameter $\times 10^4$ (cm); abscissa, solubility parameter ($\text{cal}^{0.5}/\text{cm}^{1.5}$). The bars represent the limits of the experimental errors.

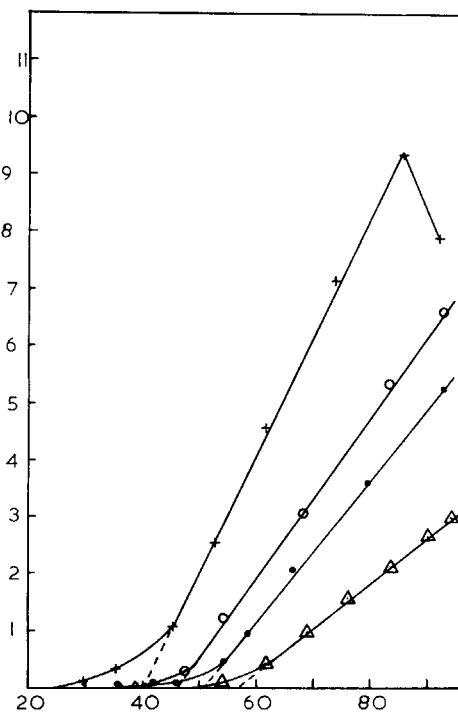


Fig. 4. Elongation of Acrilan filaments in aqueous solutions of *n*-amylamine at different temperatures: (Δ) water; (\bullet) 0.1 mole/l. *n*-amylamine; (\circ) 0.2 mole/l. *n*-amylamine; (+) 0.3 mole/l. *n*-amylamine. Ordinate, elongation (%); abscissa, temperature ($^{\circ}\text{C}$).

swelling and the solubility parameter (Fig. 3). The results do not show a well defined correlation, but there is, nevertheless, a surprising trend showing that the diameter swelling decreases as the solubility parameter of fiber and plasticizer come closer together. This unexpected result shows that as the plasticizing efficiency of a compound increases, the ability to cause radial swelling of Acrilan fibers decreases. Such results are in line with the observation made elsewhere that it is possible to find additives which do not lower the T_g but cause marked swelling (e.g., 1,5-diaminopentane).²

Mechanical Properties

The change in mechanical properties of the filaments with temperature when immersed in water or solutions of different plasticizing agents, generally followed the same pattern. A marked increase in length was observed at the T_g , and the T_g was progressively lowered with increasing concentration of plasticizer. The curves for the change in length with temperature were all parallel. In such cases, the reduction in T_g is directly proportional to the volume fraction of plasticizer in the fiber.

A few compounds however did not conform to this pattern of behavior. In these cases, the slope of the elongation curve changed with increasing concentration of plasticizing agent. A change in slope with concentration was obtained for *n*-amylamine, diaminopentane, and ethanediol (Figs. 4-6), but

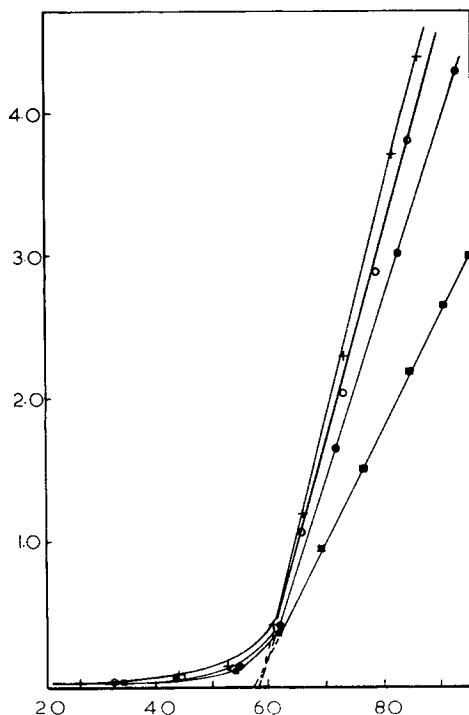


Fig. 5. Elongation of Acrilan filaments in aqueous solutions of 1,5-diaminopentane at different temperatures: (■) water; (●) 0.1 mole/l. diaminopentane; (○) 0.2 mole/l. diaminopentane; (+) 0.3 mole/l. diaminopentane. Ordinate, elongation (%) (note the expanded scale compared to Figs. 4, 6, and 7); abscissa, temperature (°C).

their effects on the T_g were different. *n*-Amylamine reduced the T_g , diamionopentane had little significant effect, but ethanediol produced a small increase in the T_g . Furthermore, at concentrations of ethanediol greater than 0.1 mole/l., the slope decreased, i.e., the fibers became stiffer.

Effect of Water on the Physical Properties of Acrilan

The action of small quantities of water in an organic solvent, benzyl alcohol, was similar to that of ethane diol in that a reduction in slope was obtained with increasing concentrations of water. In this case, however, there was a decrease in the T_g (Fig. 7). In this connection, it is interesting to note the effects of small amounts of water on polyamide fibers.¹³ Absorption of water lowers the number of interchain hydrogen bonds causing a lowering of the T_g , but at the same time the chains can pack more closely, leading to an increase in the density of the polymer.

The observations for acrylic fibers (Fig. 7) suggest that the water is restricting the movement of the polymer chains, and an increase in density is suggested by the fact that the molecular events taking place cause a reduction in the diameter of the filaments (Fig. 8). The water is clearly acting in this instance as an antiplasticizing agent, as described elsewhere.¹⁴ By virtue of their highly polar nature, the water molecules are able to pack closely and be bound to the strongly polar nitrile groups. Such a situation leads to a stiffening of the polymer chains. Analogous effects have been observed in drawn

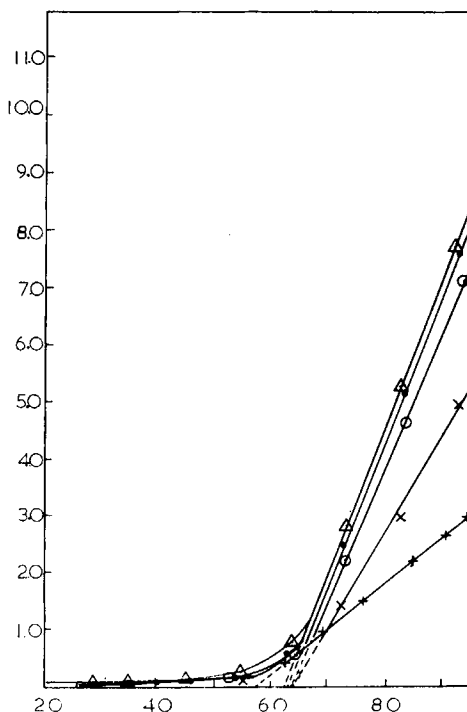


Fig. 6. Elongation of Acrilan filaments in aqueous solutions of ethanediol at different temperatures: (+) water; (Δ) 0.1 mole/l. ethanediol; (●) 0.2 mole/l. ethanediol; (○) 0.3 mole/l. ethanediol; (x) 0.4 mole/l. ethanediol. Ordinate, elongation (%); abscissa, temperature (°C).

nylon 6 fibers, where the absorption of moisture causes an increase in modulus below a temperature of 20°C and an increase in the temperature of the transition normally observed in the region of -50°C. In this instance, it was

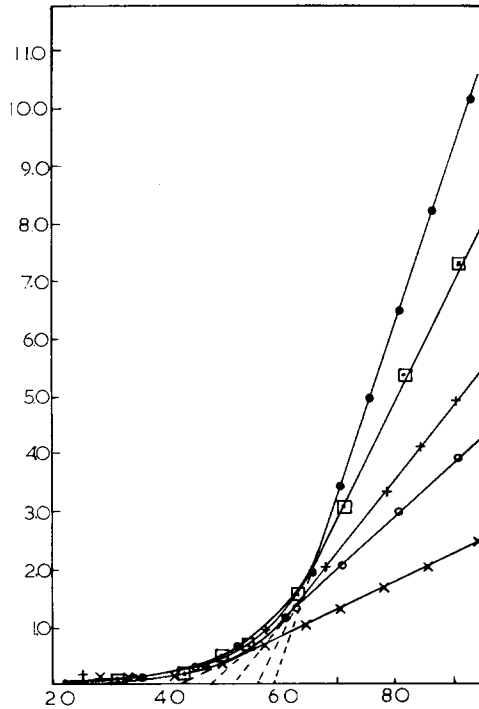


Fig. 7. Elongation of Acrilan filaments in benzyl alcohol containing different concentrations of water at different temperatures: (●) benzyl alcohol; (◻) 0.56 mole/l. water in benzyl alcohol; (+) 1.11 mole/l. water in benzyl alcohol; (○) 1.67 mole/l. water in benzyl alcohol; (×) 2.22 mole/l. water in benzyl alcohol. Ordinate, elongation (%); abscissa, temperature (°C).

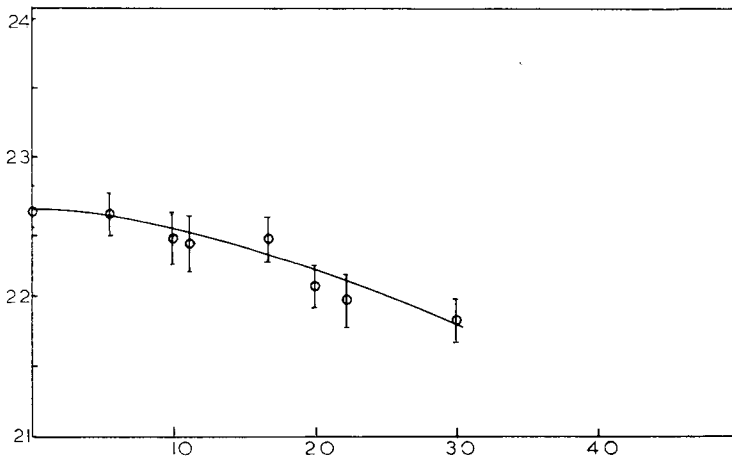


Fig. 8. Diameter of Acrilan filaments in solutions of benzyl alcohol containing water: ordinate, diameter × 10⁴ (cm); abscissa, water in benzyl alcohol (mole/l.).

suggested that the water was bonded at the lower temperature to amide groups; but when the temperature was raised to 70°C, the temperature at which the second transition occurred, the water was dissociated, and hence this transition was unaffected.

The suggestion of Kimmel and Andrews¹⁵ that the structure of polyacrylonitrile is held together by two different types of intermolecular bonding forces is particularly relevant to the results reported here. Two physical transitions were located by these workers. A transition at a lower temperature, of around 87°C, was believed to correspond to a loosening of the van der Waals bonding. In this case, the van der Waals bonding could arise from induced dipoles involving those nitrile groups not concerned in dipole-dipole associations. A further transition at around 140°C was regarded to be the result of the association-dissociation equilibrium between nitrile dipoles on adjacent chains.

If it is assumed that this view is correct and that the plasticizing agent reacts with intra- or intermolecularly associated nitrile dipoles, it would be expected that the greater the contribution of the polar forces in the plasticizer to its cohesive energy, the greater would be its disruptive effect on the structure of the filaments. This should lead to swelling of the fibers and a reduction in the T_g . The results in this paper show that this is not the case, and it is necessary to explain why the swelling diminishes when the plasticizing ability of the plasticizing molecules increases (Figs. 2 and 3).

One explanation may be given by considering the intensity of the interactions between the nitrile dipoles and the plasticizing agents. It is apparent (from Fig. 3) that those agents for which polar forces make a small contribution to the cohesive energy are the most effective swelling agents. If it is assumed that they interact only with those nitrile dipoles not involved in intermolecular association, a situation could arise in which the physical interaction between these nitrile dipoles and plasticizing molecules is strong enough to reduce the inductive effect of the nitrile dipoles on the surrounding molecules. The intensity of the van der Waals forces would be reduced and swelling would follow. At the same time, the chain stiffness in the other parts of the fiber, caused by the association of intermolecular dipoles, would be little affected and the T_g would not change. Evidence of deep-seated morphologic changes on Acrilan caused by a reagent which did not affect the T_g has already been reported.²

Plasticizer molecules of greater polarity could interact with associated nitrile dipoles. Since these are responsible for the chain stiffness, such an interaction would enable the fiber to be extended more easily, i.e., the T_g will be reduced. The reduction in the inductive effects of those nitrile dipoles involved in this process will not be as great as in the former case, since one plasticizing molecule will be intimately involved with both of the separated nitrile dipoles. The reduction in the van der Waals forces will be less, and the plasticizer will tend to hold the polymer chains together with a lower intensity than the original nitrile dipole. Consequently, although the relative ease of movement of one polymer chain past another is increased, their lateral separation is still prevented and the swelling is restricted. This suggestion is supported by the results obtained using plasticizing molecules with two polar groups, where a strong direct association of each polar group with one nitrile

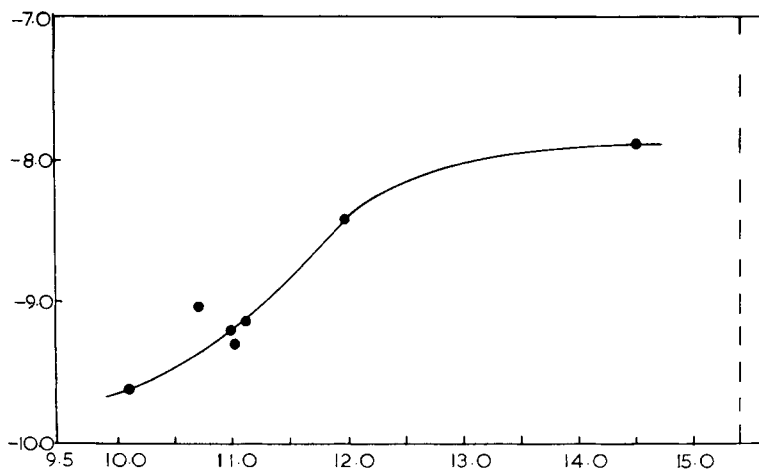


Fig. 9. Relationship between the diffusion coefficient of C.I. Disperse Orange 3 into Acrilan filaments containing 0.5 mole/kg of different plasticizing agents and their solubility parameter: ordinate, $\log_{10} D$ (cm^2/min); abscissa, solubility parameter ($\text{cal}^{0.5}/\text{cm}^{1.5}$).

dipole is possible. When the difunctional plasticizers are not long molecules, this will have the effect of reducing the molecular motion of the polymer chains, but will still cause some reduction in the van der Waals forces. In fact, one difunctional agent discussed here, ethanediol, has the effect of causing a small increase in the T_g which is accompanied by swelling of a similar magnitude to that encountered with most of the plasticizing agents which caused a reduction in the T_g . Very marked swelling was obtained with 1,5-diaminopentane, but the elongation was less than that caused by other compounds, and there was very little change in T_g .

The importance of the changes in T_g in controlling the dyeing process is shown in Figure 9. The increase in the diffusion coefficient of C.I. Disperse Orange 3 due to the presence in the fiber of equimolar concentrations of plasticizer is related to the solubility parameter of the plasticizer. The results follow the same trend as encountered with the reduction in T_g rather than the swelling behavior. Confirmation of the overriding influence of the T_g on dyeing is given by the reduction in the diffusion coefficient of C.I. Disperse Orange 3 which is caused by a difunctional carrier known to increase the T_g .²

CONCLUSIONS

It may be concluded that polar forces govern the plasticization of Acrilan fibers. Swelling and plasticization do not go hand in hand for this substrate, and the dyeing process is controlled by the plasticization of the fiber rather than the swelling.

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