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Polymer-Bromine Interactions. I. Interactions with Polyacrylonitrile

Menachem Lewin[a]; Hilda Guttman[a]; Yechiel Naor[a]
[a] School of Applied Science and Technology Hebrew University and Israel Fiber Institute Jerusalem, Israel

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POLYMER–BROMINE INTERACTIONS.
I. INTERACTIONS WITH POLYACRYLONITRILE

MENACHEM LEWIN, HILDA GUTTMAN, and YECHIEL NAOR

School of Applied Science and Technology
Hebrew University and Israel Fiber Institute
Jerusalem, Israel 91080

ABSTRACT

The present paper deals with the interactions of bromine with polyacrylonitrile (PAN). Kinetics and equilibria of the sorption of Br_2 on PAN were studied at a concentration range of 0.01-0.1 mol/L and a temperature range of 25-40°C. Two kinds of sorption were found: a "reversible" sorption removable by water and an "irreversible" sorption removable by aqueous ammonia solutions. The irreversibly sorbed bromine is presumably linked by charge transfer to the nitrile groups of the PAN, as evidenced by UV spectra. The irreversible sorption follows the reversible sorption and is slower. Partition coefficients obtained from the linear Freundlich isotherms increased with temperature and, at 40°C, the values obtained were 97, 65, and 32 L/kg for the total, irreversible, and reversible sorptions, respectively. At 25°C the chemical potential, enthalpy, and change in entropy for the irreversible sorption were - 2.0 kcal/mol, 9.4 kcal/mol, and 38 $\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. Effects of a 6-day Br_2 treatment and ammonia rinse were: decrease in dry T_g from 74.5 to 61°C and in water from 38 to 35°C; no significant decrease in $\bar{M}_w$; decrease in tensile strength measured after the bromine stage, and improvement after ammonia stage; increased swollen dimensions from 57% in water to 75%; and stabilization of swollen dimensions upon drying. The results support the existence of two phases in the less ordered regions of PAN.

INTRODUCTION

Bromine can interact with polymers in several ways, depending on the reaction conditions. At alkaline and neutral pH, bromine exists in water in the forms of hypobromous and hydrobromic acids and their salts [1]. HOBr and BrO^- are highly oxidative as has been shown for cellulose, in which ketone, aldehyde, and carboxyl groups are formed, depending on the pH [2, 3]. Below pH 2, virtually only molecular bromine exists in aqueous solutions. This is a relatively small nonpolar and hydrophobic molecule with a solubility parameter of 11.5. Its oxidative function is limited and slow. Molecular bromine is highly effective under appropriate conditions in addition and substitution reactions. The present paper is, however, limited to physicochemical interactions between bromine and polymers.

The interactions between aqueous bromine and cellulose have been described [4-8]. A reversible sorption of bromine on the glycosidic oxygens of the cellulose, i.e., a charge-transfer complex, was found and its behavior according to the Langmuir isotherm was established. An accurate method for the assessment of the accessibility of the less-ordered regions (LOR) of the cellulose was based on the sorption, and correlated with IR and x-ray data [4, 5]. Upon increasing the concentration of the bromine above 0.02 mol/L, crystallization of the cellulose took place. The rate of the crystallization was first order both with respect to the concentrations of the bromine and of the less-ordered regions of the cellulose. The crystallization mechanism postulated was based on assuming bridges were formed by the bromine molecules with glycosidic oxygens of the adjacent chains, which brought about the alignment of the chains into quasiliquid-crystalline domains, which crystallized upon removal of the bromine. Similar bridges were observed for the bromine-dioxane and bromine-acetone systems which contain long chains built up of alternating acetone or dioxane and bromine molecules [9]. In regenerated cellulose it was discovered that prior to crystallization, a pronounced decrystallization effect takes place [7, 8]. This indicates an additional effect of the hydrophobic bromine molecule of disrupting the van der Waals links between the cellulose chains in rayon [10].

In view of the above complex interactions between bromine and cellulose, it was of considerable interest to investigate possible interactions with synthetic polymers. Whereas the sorption of iodine on polyamides [11-13] and polyacrylonitrile (PAN) [14, 15] has been described in the literature, no information could be found on the physicochemical interactions of many synthetic polymers with bromine. Preliminary studies indicated high sorption of bromine on polyethylene terephthalate, polypropylene, and polyamides [16, 17]. In the following, the interactions of bromine with polyarylonitrile are investigated.

EXPERIMENTAL

The PAN used in this study was in the form of Acrylan (H-16) fibers produced at Israel Chemical Fibers, Ltd., Ashdod, Israel. It is composed of 95% acrylonitrile and 5% vinyl acetate. The diameter of the dry fibers is 0.014 mm.

Bromine Sorption Measurements

Samples of the polymer were shaken in flasks containing bromine water solutions of various concentrations at pH 2, at a series of temperatures, and for various time periods. The fiber:water ratio was 1:100 in all cases. Bromine-resistant silicone grease was used for the ground-glass stoppers which were firmly held in place by stainless steel springs. After predetermined times the flask was removed from the shaker and its liquid content was divided into two equal portions. One portion constituted the supernatant liquid and the other contained the remaining liquid and all the polymer. Both portions were titrated with arsenite and iodine [4, 5].

The concentrations of bromine in the sorption experiments are expressed in mmol/L in the solution (C_B) and in mmol/kg in the polymer (C_f).

If C_0 is the initial concentration of bromine, C_B is the concentration in the portion of the solution without the polymer, and C_2 is the concentration of bromine in the portion with the polymer, then the total sorption is

$$C_f = \frac{100(C_2 - C_B)}{2} \text{ mmol/kg}$$

whereas the irreversible sorption is

$$C_f = C_0 - \frac{100(C_B + C_2)}{2} \text{ mmol/kg.}$$

The diffusion coefficients of bromine into the polymer were determined from the half-time values of sorption and the diameter of the fibers by the equation [18, 19]

$$D = \frac{0.04919}{t_{1/2}/l^2}, \tag{1}$$

where D is the diffusion coefficient (assumed constant) and l is the fiber diameter. The half-time value was determined from a plot of M_t/M_∞ against time, where M_t is the amount of bromine sorbed at time t and M_∞ is the amount sorbed at equilibrium. Both are expressed in mmol/kg.

The Partition Coefficient

It was found in preliminary experiments that, for the sorption of bromine on PAN as well as on several other polymers studied [17], the Freundlich isotherm $C_f = KC_B{}^n$, where $n = 1$, applies. Thus, from the slopes of the plots of C_f vs C_B at equilibrium, the partition coefficients, K, are obtained. The chemical potential ($\Delta\mu_p{}^\circ$), the enthalpy ($\Delta H_p{}^\circ$), and the entropy ($\Delta S_p{}^\circ$) of partition are given by

$$\Delta\mu_p{}^\circ = -RT \ln K, \tag{2}$$

$$\Delta\mu_p{}^\circ = \Delta H_p{}^\circ - T\Delta S_p{}^\circ, \tag{3}$$

$$\frac{\partial\left(\dfrac{\Delta\mu_p{}^\circ}{T}\right)}{\partial\left(\dfrac{1}{T}\right)} = \Delta H_p{}^\circ. \tag{4}$$

Assuming $\Delta H_p{}^\circ$ to be constant in the temperature range 25-40°C, integration of Eq. (4) yields

$$\frac{\Delta\mu_p{}^\circ}{T} = \frac{\Delta H_p{}^\circ}{T} + C. \tag{5}$$

$\Delta H_p{}^\circ$ is obtained from plots of $\Delta\mu_p{}^\circ/T$ against T^{-1} for a range of temperatures. $\Delta S_p{}^\circ$ is then obtained from Eq. (3). From this value of the enthalpy of partition of bromine between water and polymer, values for the enthalpy of the solution of bromine in the polymer can be calculated from

$$\Delta H_p{}^\circ = -\Delta H_{\mathrm{sw}}{}^\circ + \Delta H_{\mathrm{sp}}{}^\circ, \tag{6}$$

where $\Delta H_{\mathrm{sw}}{}^\circ$ and $\Delta H_{\mathrm{sp}}{}^\circ$ are the enthalpies of the solution in water and polymer, respectively.

$\Delta H_{sw}{}^{\circ}$ is determined from Eqs. (7) and (8) [20]:

$$\Delta\mu_{sw}{}^{\circ} = \lim_{\rho_s \to 0} [-RT \ln (\rho_s{}^{l}/\rho_s{}^{g})]_{eq}, \tag{7}$$

where $\rho_s{}^{l}$ and $\rho_s{}^{g}$ are equilibrium molar concentrations of the solute in the liquid and gaseous phase, respectively.

$$\frac{\partial\,(\Delta\mu_{sw}{}^{\circ}/T)}{\partial\left(\frac{1}{T}\right)} = \Delta H_{sw}{}^{\circ} \tag{8}$$

$\Delta\mu_{sw}{}^{\circ}$ was calculated for bromine in water at several temperatures using vapor pressure and bromine solubility data available in the literature. A value for $\Delta H_{sw}{}^{\circ}$ of -8.12 kcal/mol was obtained.

The molecular weight of the PAN was determined viscometrically on dimethylformamide solutions by the Mark-Houwink-Sakurada equation with $K = 4 \times 10^{-4}$ and $a = 0.75$ [11, 21].

The glass transition temperature (T_g) was determined by measuring the elongation of single fibers at a series of temperatures under a load of 2.34 g.

Swelling values were calculated from the change in the diameters of the fibers. The diameters were measured according to the ASTM D-13 method with a projection microscope at a magnification of 500. Diameters of 50-100 fibers were measured for each swelling value.

Tensile strength was determined with an Instron tester at a rate of strain of 10 cm/min and as an average of measurements on 15 fibers.

RESULTS AND DISCUSSION

Reversible, Irreversible, and Total Sorption

A considerable preferential sorption of molecular bromine from bromine water on PAN is observed in Fig. 1. This is to be expected from the solubility parameter values which are 23.7, 11.5, and 15.4 $(\text{cal/cm}^3)^{1/2}$ for water, bromine, and PAN, respectively [21].

The sorbed bromine appears to be composed of two parts which were determined analytically. The "reversibly" sorbed bromine which can be washed out by soaking the polymer in water and dilute alkali or reduced by sodium arsenite or sulfite. This part of the sorbed bromine behaves in a way similar

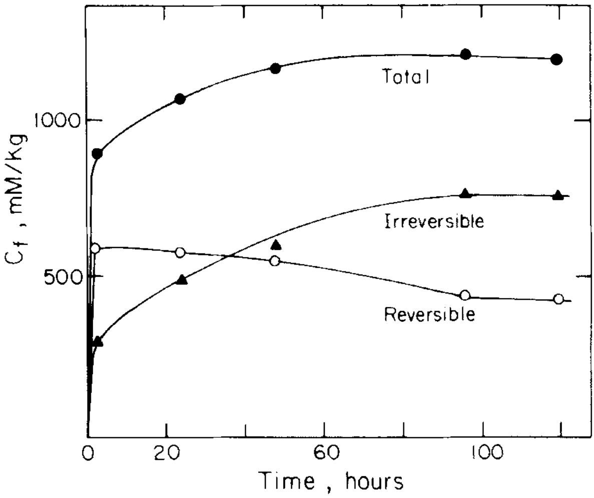

FIG. 1. Sorption of bromine from aqueous solution on PAN fiber as a function of time at 25°C. Concentration of Br_2: 0.037 mol/L.

to the bromine sorbed on polypropylene [17]. This bromine is "dissolved" in the polymer, which behaves as a solvent.

The "irreversibly" sorbed portion defines the bromine that cannot be removed by the above means and, after prolonged washing, still manifests itself in the deep yellow-brown discoloration of the polymer. In order to remove it, a special reagent has to be used which is capable of penetrating the polymer and of interacting with the sorbed bromine *in situ.* Such a reagent was found to be aqueous ammonia solution [17] in which, due to the equilibrium

$$NH_3 + H_2O = NH_4OH, \tag{9}$$

a considerable concentration of the NH_3 moiety exists. NH_3 is a small nonpolar and un-ionized molecule and it was found to penetrate relatively rapidly into the PAN and reduce the bromine molecules according to the overall reaction [9]

$$8NH_3 + 3Br_2 \longrightarrow 6NH_4Br + N_2. \tag{10}$$

This is an exothermic reaction which proceeds rapidly in the polymer phase.

The sum of the reversible and irreversible sorptions is termed "total sorption." The equilibrium state of the total and irreversible sorptions is reached at 25°C after ~100 h of contact with the bromine solution (see Fig. 1) which is a considerably longer time than in the case of cellulose [4, 5], polyethylene terephthalate, or polypropylene [16, 17]. The maximum of the relatively rapid reversible sorption is, however, reached after 2 h when it starts to decrease slightly until it reaches a steady-state concentration in the polymer. The irreversible sorption is slower and at equilibrium constitutes 63% of the total sorption under the experimental conditions of Fig. 1. It appears, therefore, that the polymer is first swollen by the aqueous bromine solution, enabling bromine to dissolve in the less closely packed domains of the amorphous phase of the polymer. In the second stage this dissolved bromine diffuses into the more highly ordered region, possibly the amorphous oriented regions between the small crystallites [22]. A similar two-stage mechanism has already been postulated for dyeing of acrylic fibers [23]. It is assumed that, during the second slow sorption stage, a part of the sorbed bromine is attached by charge transfer to the nitrile groups of the PAN and becomes immobilized, thus forming the irreversible portion of the sorbed bromine [9].

Diffusion

The data on the diffusion of bromine into PAN, obtained from Fig. 2, point in a similar direction. The diffusion coefficient (*D*) determined for the total

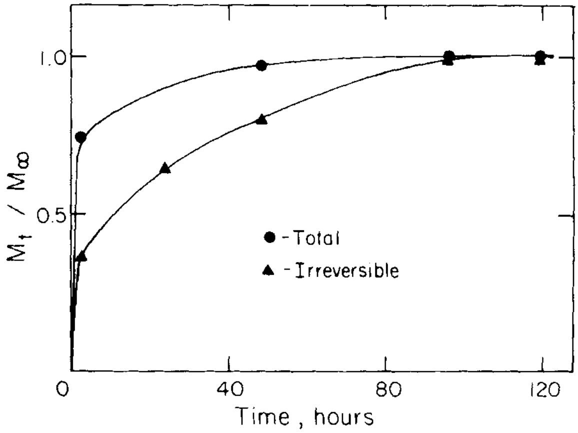

FIG. 2. Kinetics of diffusion of bromine into PAN.

sorption was 3.3 X 10^{-11} cm^2/s at 25°C, which is lower by two orders of magnitude than that for polyethylene terephthalate, nylon 6, or polypropylene [17]. The D value for the irreversible sorption is lower by an order of magnitude than the total sorption, e.g., 4.1 X 10^{-12} cm^2/s. The half-time values for the diffusion are 9.6 and 1.2 h for the irreversible and total sorptions, respectively.

The Thermodynamic Parameters

The Freundlich sorption isotherms in Figs. 3, 4, and 5 represent results obtained for a series of bromine concentrations of 0.007-0.08 mol/L at 25, 35, and 40°C. The slopes of the straight lines represent the partition coefficients of the bromine between water and PAN which are also, in this case, the equilibrium constants K. The K values for the irreversible sorption are, at all temperatures investigated, higher than those for the reversible sorptions, and the ratio K_{irr}/K_{rev} is 1.7 for 25 and 35°C, but increases to 2.03 at 40°C. The basic two-stage mechanism of the sorption remains unchanged in the whole temperature range investigated.

The K values increased markedly with temperature and, at equilibrium between PAN and a saturated bromine solution (Fig. 5), 3.1 mol Br_2 are sorbed per kg PAN. A similar temperature dependence was observed upon dyeing.

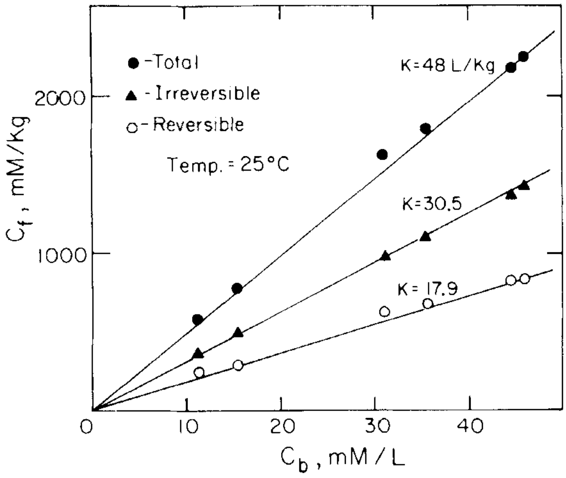

FIG. 3. Equilibrium sorption of bromine on PAN at several concentrations at 25°C. K = partition coefficient.

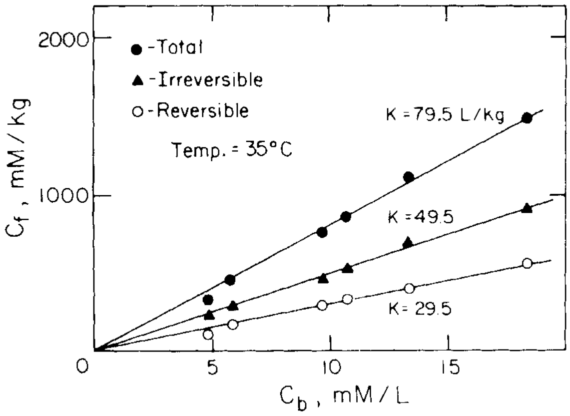

FIG. 4. Equilibrium sorption of bromine on PAN at 35°C.

Peters and Wang [24] postulated a correlation between the area under the tan δ of the polymer and the saturation dye uptake from 20°C to the dyeing temperature. The dye uptake is thus assumed to be related to the proportion of the mobile or rubberlike chain segments which becomes highly significant when temperatures approach and surpass the T_g. The T_g of the wet PAN

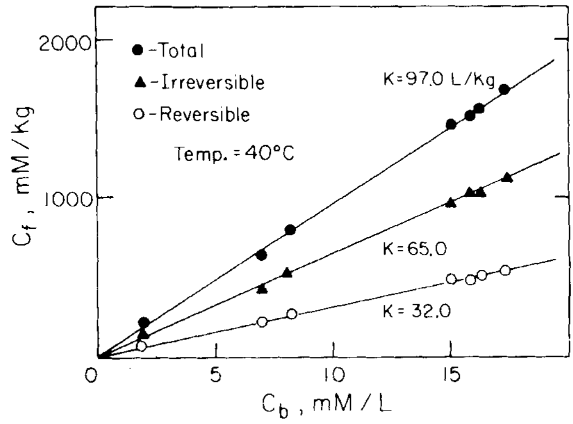

FIG. 5. Equilibrium sorption of bromine on PAN at 40°C.

TABLE 1. Thermodynamic Equilibrium Data of Bromine Sorption on PAN

Function	Temperature, °C	Reversible sorption	Irreversible sorption	Total sorption
K, L/kg	25	17.9	30	48
	35	29.5	49.5	79.5
	40	32.0	65.0	97.0
$\Delta\mu_p{}^\circ$, kcal/mol	25	-1.7	-2.0	-2.3
	35	-2.1	-2.4	-2.7
	40	-2.2	-2.6	-2.9
ΔHp°, kcal/mol	25-40	8.1	9.4	9.2
$\Delta S_p{}^\circ$, $\mathrm{cal \cdot mol^{-1} \cdot K^{-1}}$	25	32	38	39
	35	34	39	39
	40	33	39	39

fibers used in this study was found to be 38°C (see Fig. 9), i.e., within the temperature range investigated, which explains the increase in the K values with temperature.

The values of the chemical potential of the partition ($\Delta\mu_p{}^\circ$) obtained by Eq. (2) are listed in Table 1. This table also contains the values for the enthalpy of partition $\Delta H_p{}^\circ$ obtained by using Eq. (5) and the plots in Fig. 6, as well as the values for the entropy change, $\Delta S_p{}^\circ$, by Eq. (3).

The chemical potential, which is the driving force for the sorption process to proceed spontaneously, is ~-2000 cal/mol, which is considerably higher than the value of -816 cal/mol obtained for the sorption of bromine on cellulose [5].

The positive value of the enthalpy indicates an overall endothermic process of the transfer of the bromine molecules from water to polymer. When the enthalpy of solution of bromine in water is taken into account according to Eq. (6), values of $\Delta H_{\mathrm{sp}}{}^\circ$ of 0.0, 1.3, and 1.2 kcal/mol are obtained for the enthalpy of solution of bromine in the polymer for the reversible, irreversible,

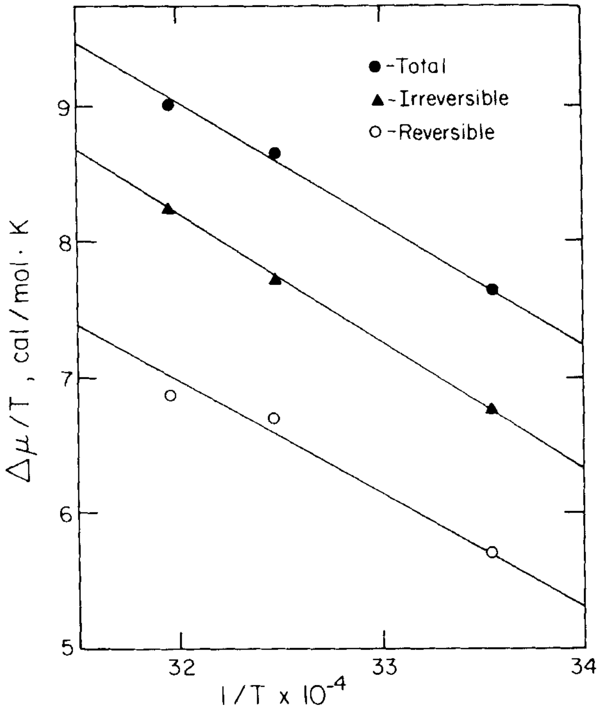

FIG. 6. $\Delta\mu/T$ versus $1/T$ for the reversible, irreversible, and total sorption of bromine on PAN fibers.

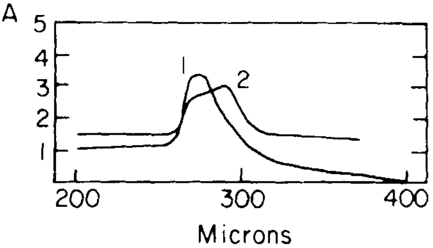

FIG. 7. UV absorption (A) of bromine dissolved in DMF (Curve 1) and of PAN containing reversibly sorbed bromine dissolved in DMF (Curve 2).

and total sorptions, respectively. The enthalpy of solution is composed of at least two terms, the enthalpy of mixing of the bromine "solvent" with the polymer (positive) and the enthalpy of the formation of the charge-transfer complex between bromine and the nitrile groups of PAN (negative sign). The present results do not permit the separate determination of these two enthalpies. It appears that the enthalpy of the complex formation will be relatively low since, in the complex between acetonitrile and bromine, the existence of molecular bridges has been suggested [9]. Such bridges have not been suggested for iodine-nitrogen complexes for which high enthalpies of formation of 7-12 kcal/mol were found. The existence of the charge-transfer complex between bromine and the nitrile groups of the PAN samples used in the present study is indicated by the shift in the UV band at 270 nm of bromine in DMF solution to 290 nm for bromine bound to PAN in the same solvent (see Fig. 7). No difference in the IR spectrum was detected between untreated and bromine-containing PAN. It is of interest to note that the IR spectrum of PAN was also found to remain unchanged after sorption of iodine [14]. The positive entropy changes calculated by Eq. (3) are typical for polymer-solvent mixing [25-28] since segmental mobility and randomness of the polymer are increased due to the separation of polymer chains by the solvent.

Swelling

The PAN fibers swell strongly when wet with water or with ammonia-containing water (see Table 2), and an increase of 57% in diameter is observed. The presence of increasing amounts of bromine in the water brings about corresponding increases in swelling so that an additional 18.2% increase in the average fiber diameter was observed at a bromine concentration of 0.083 *N*. It appears that the bromine molecules penetrated additional domains of the fiber that were inaccessible to water and ammonia. While water swelling is reversible and the fiber diameter returns to its original dry value upon air drying, the bromine and ammonia treatment of the fibers produces a permanent effect. Upon drying in air, the fiber remains fully swollen and half of the swelling remains even after drying at 110°C, i.e., above the T_g.

Molecular Weight

The intrinsic viscosity of untreated and treated PAN was determined at 25°C. The treatment consisted of a 6-day immersion of the fibers in 0.083 mol/L Br_2, immersion for 15 min in a concentrated ammonia solution, all at 25°C, rinsing in water, and air drying. Values of intrinsic viscosities of 1.44

TABLE 2. Effect of Bromine and Ammonia Treatments on Swelling of PAN

Treatment	Diameter, μm
Dry fiber	14
Wet, in water	22
Wet, in concentrated ammonia	22
Wet, 5 days in 0.326 N Br_2 solution	17
Wet, 5 days in 0.0521 N Br_2 solution	20
Wet, 5 days in 0.083 N Br_2 solution	26
As above, treated with concentrated ammonia	26
As above, air dried	26
As above, dried at 110°C	20

($\bar{M}_v$ = 55 130) and 1.47 ($\bar{M}_v$ = 56 700) were obtained for the treated and untreated fibers, indicating that no significant degradation took place in the prolonged treatment in bromine water.

Tensile Strength

The tensile strength of the PAN fibers decreased upon treatment with bromine, the main decrease occurring in the range of 0.012-0.05 N (see Fig. 8). These samples, which were rinsed in water and dried at 50°C, still contained irreversibly sorbed bromine in amounts corresponding to the concentrations of the bromine solution used in the treatment. When, however, the bromine-PAN complex was decomposed by the ammonia treatment and the bromine reduced, the tensile strengths were very significantly higher (Fig. 8, upper curve).

Similar results were obtained on polyamide fibers [17]. Since the molecular weight did not change significantly upon bromine treatment, it is evident that the drop in the tensile values decreased due to changes in the structure.

Glass Transitions

The treatment of the PAN fibers with bromine water, and subsequently with concentrated ammonia, brings about a decrease in the dry T_g from 74°C

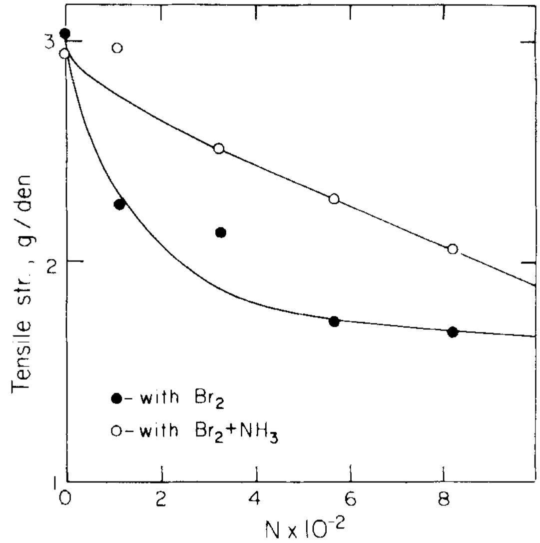

FIG. 8. Effect of bromine concentration with and without subsequent ammonia treatment on tensile strength of PAN fibers. Time of treatment in bromine solutions: 6 d at 25°C. Rinsing in water or concentrated ammonia at 25°C, drying at 50°C.

for the untreated fiber to 61°C (see Fig. 9). The T_g of the fibers measured in water was found to be 38°C, i.e., 36°C lower than that of the dry fiber. A similar decrease in T_g upon wetting of PAN was observed by Rosenbaum [29].

The corresponding T_g measured after bromine and ammonia treatments (see Fig. 9) was 35°C. These results, as well as the results obtained on swelling (Table 2), point to the possibility of the existence of at least two noncrystalline phases in the fiber. The first phase is penetrable by water, and hydrogen bonds are broken. The distances between chains, i.e., the free volume, and the segment mobility are increased along with a decrease in the cohesive energy density. This is expressed in the pronounced swelling and the drastic decrease in T_g upon wetting. It is in this phase that the reversibly sorbed bromine penetrates first and accumulates.

The above changes are not permanent, and they eventually disappear upon drying. Treatment with bromine water brings about penetration into a new, more closely packed phase and consequently a further sizable increase in swelling and a corresponding decrease in T_g. The extent of this effect increases with increasing bromine concentration and temperature, which enhances the amount of bromine irreversibly sorbed into domains of increased

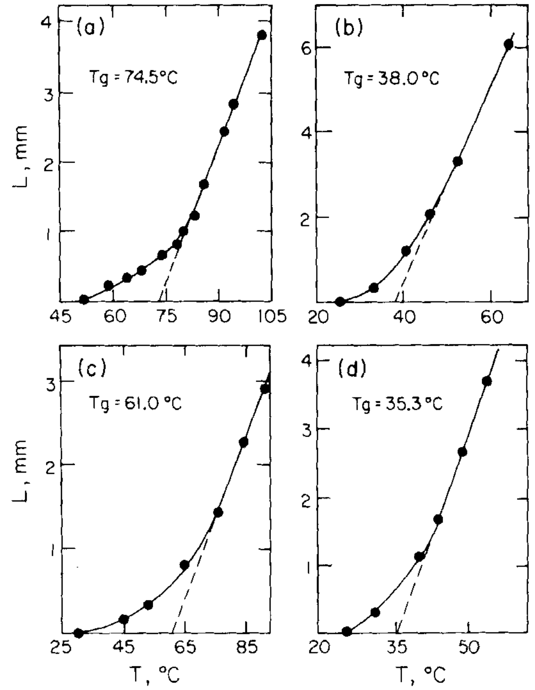

FIG. 9. Elongation versus temperature of dry and wet PAN fibers under a load of 2.34 g. (a) Dry, untreated fibers. (b) Untreated fibers in water. (c) Fibers treated in 0.1 mol/L Br_2 for 5 d, neutralized for 15 min in 25% ammonia solution, rinsed in water, and dried. (d) Similar to (c), measured while immersed in water.

order [15]. It appears that the bromine molecules disrupt a part of the interchain dipole interactions of nitrile groups and produce relatively stable charge-transfer complexes, but this is a slow process. The low diffusion coefficient of the irreversible sorption indicates relatively close packing, possibly due to high chain orientation in the phase involved.

The existence of oriented noncrystalline domains consisting of partly extended chains between microfibrils has been postulated by Prevorsek for PET [30, 31]. It has been stated "that it is these domains that are plasticized and restructured as a result of polymer-solvent interactions and therefore have a major effect on the properties of the solvent-treated fibers both in the presence of the solvent and after its removal" [32]. The penetration of the bromine into these domains brings about increases in the distance between the chains and facilitates local disorientation effects and chain slippage, which explains the decrease in tensile strength in Fig. 8.

A further change in the structure is caused by ammonia treatment of the bromine-containing polymer. The reduction of the sorbed bromine, an exothermic process, causes local heating of small domains inside the polymer. The nitrogen gas (Eq. 10) evolved in the process immediately expands and produces sizable pressures within these domains. The plasticized chain segments will be forced to move sideways (away from the center of the N_2 evolution) and pores will be formed. Thus the structure of the noncrystalline regions will be rearranged. The chains will occupy new compact positions around the pores, and new interactions between nitrile groups will be formed. This new structure will probably be less oriented and less ordered than the original, as evidenced by the lower dry and wet T_g values of the treated fiber. On the other hand, this new structure restores a part of the tensile strength lost by the bromine penetration. Furthermore, it appears to stabilize the structure swollen in bromine water upon air drying, and even heating at a temperature of 50°C above the T_g causes only a partial collapse of the swollen sample.

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