

Wholly Aromatic Polyamide-Hydrazides. V. Preparation and Properties of Semipermeable Membranes from Poly[4-(terephthalamino) Benzoic Acid Hydrazide]

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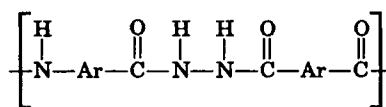
SYNOPSIS

Effects of several processing parameters on the properties of poly[4-(terephthalamino) benzoic acid hydrazide] semipermeable membranes were investigated. The membranes were prepared using a polymer phase inversion method that consisted of the following sequence of steps: casting of thin, neutralized polymer solution layers on suitable solid support; thermal treatment of the obtained layers to form viscous liquid protomembranes; coagulation of the protomembranes into solid semipermeable membranes; and, when that was additionally desired, posttreatment of the obtained membranes in order to further affect their final separation properties. The processing parameters investigated included temperature and time of exposure to thermal treatment during the preparation of protomembranes, nature of the employed medium, time of exposure, and temperature of the posttreatment of coagulated membranes. In addition, particular attention was devoted to the effect of polymer molecular weight on the properties of the membranes, and for that purpose a series of five polymer samples with molecular weights that ranged from about 17,000 to about 64,500 was prepared using the previously described viscometrical method to monitor the polymer forming polycondensation reactions. The results obtained showed that membrane performance was very much influenced by all of the examined processing variables and that products with considerably different properties could be obtained from the same polymer sample by using different processing parameters. Thus, the use of higher temperatures and longer exposure times in the protomembrane forming thermal treatment step gave higher rejection and lower permeability of the finished membranes, although there seems to exist limiting "ceiling conditions" above which this trend rather abruptly ceases to continue any further. It appears that these conditions correspond to the onset of irreversible changes, either in the polymer chemical structure or in the membrane supermolecular organization. Posttreatment of the prepared membranes was found essential for useful properties in the single-stage separation applications, which require high membrane selectivity. Of the investigated possibilities, annealing in boiling deionized water was crucial, while exposure to concentrated acids was also important in the case of HCl but rather deleterious in the case of H₂SO₄. Most significantly, the membrane properties clearly depended on the polymer molecular weight, and it was found that there was a critical polymer molecular weight above which this dependence ceased to be important for practical purposes. It is suggested that this may be a general phenomenon, characteristic for all membrane forming polymer materials, and a possible explanation of its nature is tentatively offered.

INTRODUCTION

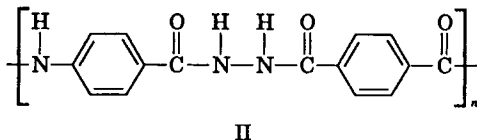
Wholly aromatic polyamide-hydrazides of the general structure I have attracted considerable research

attention in recent years as membrane forming polymers.¹⁻⁶



I

The first successful preparation of a series of semi-permeable membranes from one of these polymers, the poly[4-(terephthaloylamino) benzoic acid hydrazide], PTABH, II, was reported in 1971 by McKinney and Rhodes.¹⁻³



These authors developed a procedure that used this polymer solution in *N,N*-dimethylacetamide, DMA, (6–20 wt %) to yield thin asymmetric membranes that showed excellent characteristics when tested under the reverse osmosis conditions either with NaCl–H₂O feed solutions or with natural seawater.^{1,2} The membranes obtained also had high selectivity (> 99% rejection) toward other solutes, particularly MgSO₄, NH₄Cl, HCl, fructose, or polyethylene glycol,² and at these high rejections they allowed permeant fluxes from 3.4 to 6.8 L/m² h.² In addition, these membranes also exhibited excellent mechanical properties (modulus of about 250,000 psi and yield stress of 7150 psi)¹ and very good chemical resistance (especially in the high pH range).¹

Following this work, Rosenblatt and co-workers⁵ performed an extensive investigation of the effects of various processing conditions on the properties of seamless tubular and flat membranes from another polyamide-hydrazide that was prepared by polymerizing a mixture of 80 parts of *m*-aminobenzhydrazide (*m*-ABH) and 20 parts of *p*-aminobenzhydrazide (*p*-ABH) with a mixture of 70 parts of isophthaloyl chloride (ICI) and 30 parts of terephthaloyl chloride (TCI), again in DMA as a solvent. They also showed that several different processing variables (such as casting solution composition, heating time and temperature, coagulation medium and coagulation temperature, as well as various posttreatment conditions) clearly and significantly influenced membrane performance characteristics, so that products ranging from those useful for two-stage desalination processes to those suitable for single-stage operations could be prepared by appropriately selecting the processing parameters. The results obtained indicated that under 1000 psi pressure and within the temperature range from 0 to 30°C, these membranes could on average reject above 99% of Cl⁻ ions and permit fluxes of 14.2 ± 1.3 gfd when separating either the 3.5 wt % NaCl–H₂O feed solutions or natural sea water.

Finally, most recently, a series of semipermeable

membranes was prepared from a series of polyamide-hydrazides that contained different amounts of *para* and *meta* phenylene rings.⁶ These polymers were obtained by the low-temperature solution polycondensation reactions of *p*-ABH with different mixtures of TCl and ICl chlorides, again in DMA as a solvent, and their structural characterization revealed that within the investigated series the *para*/*meta* ratio changed from 100/0 to 50/50 mol % in the increments of about 12.5 mol %. The polymers had similar average molecular weights (\bar{M}_w of about 20,000), and the membranes were prepared and tested under exactly the same experimental conditions. The results obtained showed that their properties were significantly dependent on the polymer composition, so that increase in *para*-phenylene content clearly resulted in corresponding increase in percent Cl⁻ rejection and also in simultaneous decrease in the permeant flux. It was suggested that such behavior was a consequence of polymer chain flexibility that can be expected to influence the regularity of segmental packing within the membrane matrix and therefore also the efficiency of hydrogen bonding between the adjacent amide and/or hydrazine groups.⁶

These results also clearly showed that within this particular polymer family, specific properties of the semipermeable membranes depended to a significant extent not only on the changes in polymer structure (which might sometimes be so fine to even seem insignificant, at least at first consideration), but also on the processing procedure and experimental conditions used for membrane preparation. The procedure used was in all cases the so-called phase inversion process,⁴ which usually consists of a sequence of several consecutive interrelated steps. First, a tractable polymer solution (with or without various possible additives, such as inorganic salts for solubility enhancement, or organic diluents for closer control of polymer phase separation process) is prepared in a good solvent for the polymer. In addition, such solvent should be reasonably volatile and also miscible with a suitable nonsolvent for the polymer. Second, a uniform (up to 150 mils thick) layer of such polymer solution is cast on a suitable support that must have smooth surface and be chemically inert and mechanically and thermally stable. Third, the cast solution layer is exposed to precisely controlled thermal treatment in order to partially evaporate the solvent and establish a concentration gradient across its depth to form the so-called protomembrane. Fourth, the protomembrane is coagulated in a nonsolvent for the polymer in order to freeze the obtained spatial structure of the layer

and to extract the remaining solvent and additives; and, finally, fifth, the resulting membrane is, if so desired, further posttreated by some suitable procedure, such as annealing at specified temperature or exposure to chemical agents or radiation, or by some other selected method, in order to improve its separation properties, most often to increase the selectivity.

This general procedure for membrane preparation is based on phase inversion⁴ of the polymer from its dissolved state to a thin solid film, and, at least in principle, it is applicable to all synthetic film forming polymers, including derivatives of cellulose, aromatic polyamides, polyhydrazides or polyamide-hydrazides, which have, until now, played the dominant roles in most of the successful membrane separation technologies. Of course, depending on the particular type and properties of the selected polymer and on desired membrane separation characteristics, specific working conditions and processing parameters for each of the preceding individual preparation steps may differ significantly, particularly in terms of the nature and the amount of solvent, nonsolvent, additives, or diluents used; duration and the extent of thermal treatment, solvent extraction, or post-treatment; composition and temperature of the coagulating medium, etc.

Thus, considering that the two major groups of factors that determine membrane properties are (1) structural features of the polymer used and (2) particular working parameters of the processing procedure, by applying proper combination of the processing parameters, it is often possible to prepare very similar membranes from quite different polymer materials, but also to tailor-make significantly different membranes from the same starting polymer sample. Since the effects of some polymer structural features on the membrane performance characteristics in the polyamide-hydrazide series (I) in which Ar and Ar' were C₆H₄ were described in the previous publication from this series,⁶ this article will focus in more detail on the results of recent investigation of the effects of membrane preparation conditions on the properties of the obtained membranes.

The reasons for this are manifold. First, it has been already clearly shown¹⁻⁶ that considerable number of preparative variables can and does influence membrane properties and that effects of these variables may be either favorably convergent or undesirably antagonistic. Second, possible effects of one of the most important polymer properties—its molecular weight—on the membrane characteristics have not attracted much of the research attention as yet, and particularly none in the family of poly-

amide-hydrazides; and finally, it was also hoped that a detailed investigation of the effects of selected preparative parameters on the properties of membranes obtained from a well-defined series of polymer samples can give more concrete guidelines for preparation of the products that would be just right for use in certain prespecified particular applications. PTABH was selected as the polymer for these investigations because it was earlier shown to be one of the most promising candidates from the aromatic polyamide-hydrazides family for some single-stage separation processes such as desalination by reverse osmosis or certain purification methods that use ultrafiltration.⁶

EXPERIMENTAL

Polymer Preparation

Five different PTABH samples having molecular weights, \bar{M}_w , of 16,900, 17,900, 19,250, 20,350, and 64,500, respectively, were prepared by a low-temperature (0–5°C) solution polycondensation reaction of *p*-ABH and TCl in DMA solvent. The preparations were carried out by adding solid TCl monomer into cooled *p*-ABH–DMA solutions, and polymer molecular weight control was achieved by using the previously described viscometrical monitoring method.⁷ Detailed description of this preparative technique was given elsewhere.^{6,7}

Polymer Characterization

The polymers obtained were characterized after isolation from neutralized DMA solutions described in the following section. Isolation was carried out by precipitation in methanol, filtration and drying, and the obtained samples were characterized by elemental analysis, infrared, and ¹H-NMR spectroscopy. The results obtained agreed well with the previously reported data,⁶ and they confirmed the expected polymer structure.

Polymer molecular weights were determined by dilute-solution viscosity measurements at 20 ± 0.5°C in DMA as a solvent.^{6,7} Solutions were prepared at room temperature, and they ranged in concentrations from 0.4 to 0.55 g/dL. Flow times were determined for each polymer at five different concentrations using Canon viscometers, which were selected to give solvent flow time in excess of 100 s. All flow times were sufficiently long to justify neglect of kinetic energy corrections and the lack of shear rate dependence was verified. Intrinsic viscosities were

determined by the usual double extrapolation of η_{sp}/c and $(\ln \eta_{rel})/c$ to zero concentration. The plots obtained were linear in all cases, and the molecular weights were calculated using the previously reported equation⁷:

$$[\eta] = 5.15 \times 10^{-4} \bar{M}_w^{0.84}$$

Polymer Solutions for Membrane Preparation

Following the completion of polycondensation reactions, about 130 mol % of the stoichiometrically required quantity of CaCO_3 was added to the resulting polymerization reaction mixtures in order to neutralize HCl, the polycondensation by-product. The mixtures obtained were warmed to about 70–80°C and stirred at that temperature for no less than 3 h. When the neutralization was completed, the resulting mixtures were vacuum filtered through a porous sintered glass filter funnel (or through a cloth filter if the viscosity was too high) to remove the CaCl_2 formed and to degas the obtained liquid filtrates. A sample of each filtrate was taken to determine polymer concentration by precipitation, isolation, washing, and weighting, and the rest of the filtrate was stored under dry nitrogen atmosphere, at room temperature and in dark, until further use for membrane preparation. In all cases polymer concentration was 7 ± 0.1 wt % and no changes in solution composition or viscosity, or polymer intrinsic viscosity could be detected during at least 6 months under these storage conditions.

Membrane Preparation

Flat-sheet PTABH membranes were prepared from the described, neutralized polymer solutions in DMA by a modification of the procedure originally developed by McKinney and Rhodes¹ and recently used in this author's laboratories.⁶ First, using a cylindrical stainless steel knife, 120- μm thick solution layers were cast on the glass supports, which had previously been treated with silver vapor. Then, these layers were thermally treated in an air-circulated electrical oven for desired periods of time at selected temperatures to allow for partial solvent evaporation and formation of liquid protomembranes. The temperature range covered in the preparations in this work was from 25 to 150°C and the treatment times extended from 5 min to 5 h. Following the thermal treatment, the protomembranes obtained were quickly coagulated in deionized water at 25°C to fix the established supermolecular structure and to allow for complete solvent extraction

from the resulting membranes. The latter would normally separate from the glass support surfaces after about 5–15 min in coagulation bath, after which about 5 h would usually be allowed for solvent extraction. Finally, when that was desired, the membranes were posttreated either by annealing in boiling deionized water or by exposure to concentrated mineral acids, such as HCl or H_2SO_4 , for selected periods of time, but usually for about 1 h. All membranes prepared in this way ranged from 2 to 8 μm in thickness, appeared perfectly transparent, showed good mechanical strength to handle, and were stored until testing in a formalin–water solution of about 5 wt % concentration.

Membrane Testing

The PTABH flat-sheet membranes were prepared in rectangular shapes of about 30 \times 25 cm in size. From these sheets six circular samples of 15.4 cm^2 each were cut out for property evaluation tests. The testing was performed in a home-made apparatus that consisted of six parallel steal chambers equipped with feed solution inlets, permeant and concentrant outlets, pipelines for feed and permeant transport, pressure regulators and control gauges, nitrogen pressure tank, and a feed solution reservoir. A schematic representation of this setup is shown in Figure 1 together with a cross-sectional view of a single testing chamber. In the chamber each membrane was placed with its active side (the side exposed to air during the thermal treatment) facing the incoming feed solution. Underneath each membrane the support was a layer of coarse laboratory filter paper, which in turn was laid on a 0.5-cm-thick sintered steal plate. Tight fitting of the chamber locks was ensured by a pair of rubbery O-ring sealants.

Constant working pressure in the testing instrument was maintained by using a nitrogen pressure tank and a system of regulating pressure gauges produced by Consolidated Controls, El Segundo, California. The feed solution was driven to the testing chambers at constant flow rate by means of a high-pressure piston pump, type N-K 31, Brau und Lube GmbH, Austria.

In all experiments performed in this work the feed solution was a 1.7×10^{-2} mol/L NaCl in water, the working pressure was 3.92×10^6 Pa, and the testing temperature range was 22–24°C. The membranes were characterized for their selectivity, by determination of the percent rejection of Cl^- ions using the volumetric AgNO_3 titration method, and for their permeability, by measuring the permeant

A: Membrane Testing Apparatus

B: Testing Chamber Cross-section

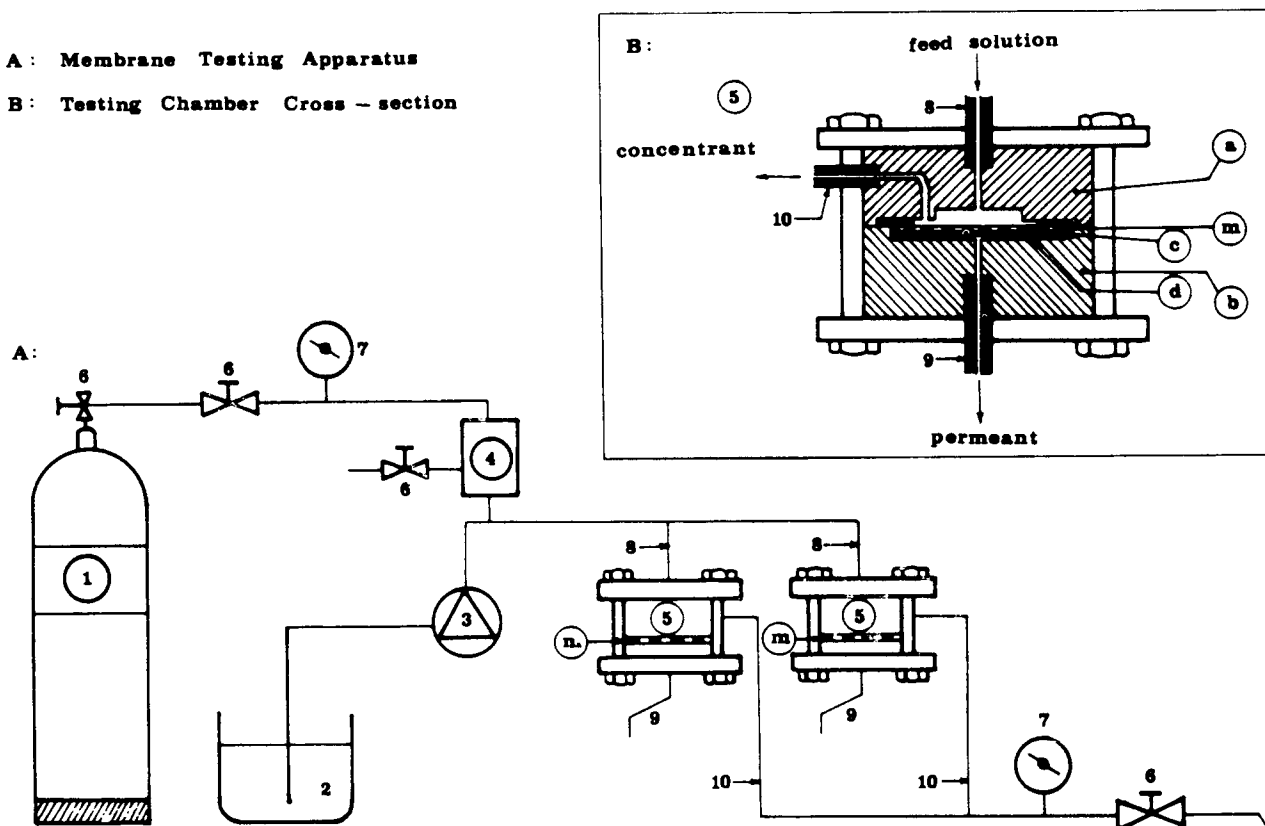


Figure 1 Schematic representation of the membrane testing apparatus used. Cross-cut view of a testing chamber is given in the window.

volume flow rate. The accuracy of these measurements was $\pm 0.05\%$ for Cl^- rejection and $\pm 0.013 \text{ cm}^3/\text{cm}^2 \text{ h}$ for the permeant fluxes.

RESULTS AND DISCUSSION

All membranes prepared in this work were tested for no less than 40 h under the same experimental conditions, which included feed solution concentration, pressure, and temperature as specified in the experimental section. In these tests they all showed similar general trend of behavior, regardless of which preparation variable had been changed and how this change was affected. Thus, all property vs. time curves obtained were exponential in character, showing first a rapid initial increase in the percent Cl^- rejection and simultaneous decrease in the permeant flux, followed by subsequent decrease in the rates of both changes and final establishment of constant asymptotic levels of both properties. This leveling off usually occurred after about 5–7 h of test.

Of many preparative parameters that may influence a membrane production process by phase inversion, only a group of those, which in our previous experience⁶ was found to exhibit the most significant effects on the obtained membrane properties, was chosen for more detailed investigation in this work. These included temperature and time of exposure to thermal treatment during the preparation of protomembranes and parameters for membrane post-treatment by either thermal annealing or by exposure to acids. In addition, for the reasons stated earlier, particular attention was devoted to the influence of the molecular weight of the polymer used.

Effects of Thermal Treatment Conditions

As described in the experimental section, after casting on glass supports, thin polymer solution layers were first exposed to thermal treatment in order to enable partial evaporation of DMA solvent and to induce spatial structuralization of the resulting concentrated solutions, which are called protomembranes. Each such treatment can be characterized

by the temperature used and by the extent of time during which a polymer solution layer was exposed to heating. In all cases in this work, dry air was circulated freely over the sides of protomembranes,

which were facing away from the casting glass supports, and the volume of the oven used was large enough to assure unrestricted evaporation of the solvent.

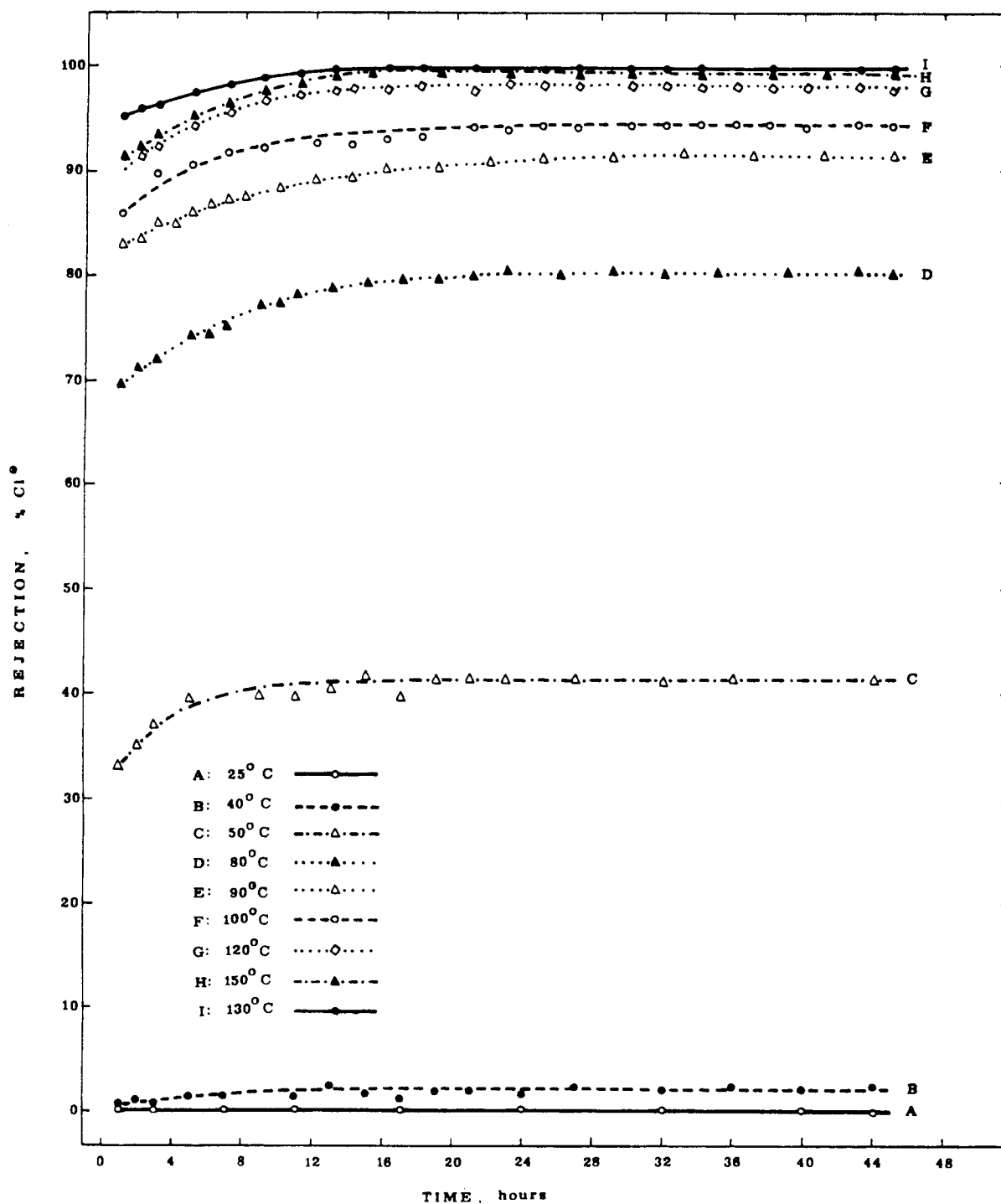


Figure 2 Rejection of Cl^- ions as a function of thermal treatment temperature. All membranes were prepared from a 7 wt % PTABH ($\bar{M}_w = 20,350$) solution in DMA, thermally treated for 1 h and posttreated for 15 min in boiling deionized water.

Effect of Temperature

It has been shown earlier by thermal gravimetric analysis that PTABH does not begin to undergo thermo-oxidative degradation until about 240°C.^{8,9} At this and higher temperatures, however, dehydrocyclization reaction takes place and polymer structure irreversibly changes into that of a corresponding polybenzimidazole.^{8,9} Therefore, in order to prevent from undesired polymer degradation, the temperature interval selected for thermal treatments in this

work was from 25 to 150°C, and at given temperature the heating times were in most cases limited to 1 h.

The effects of heating temperature and time of exposure to thermal treatment on membrane rejection and permeability are shown in Figures 2 through 4. The membranes used were all prepared from the same polymer sample that had molecular weight, \bar{M}_w , of 20,350, and all other processing parameters in their preparations were also identical: polymer solution concentration was 7 wt %, membrane coagulation was performed in deionized water at 25°C,

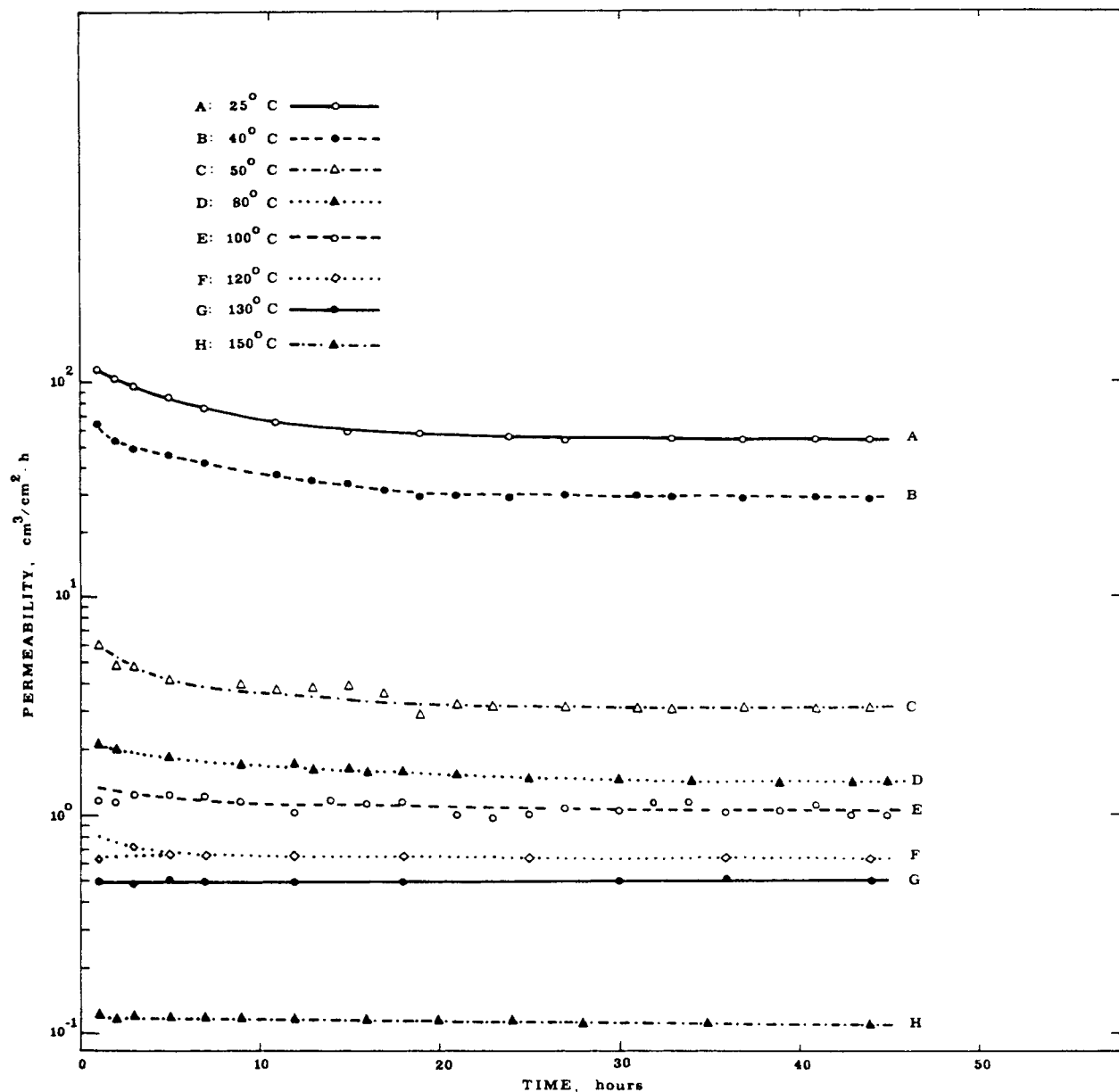


Figure 3 Permeant flux as a function of thermal treatment temperature. All membranes as described in Figure 2.

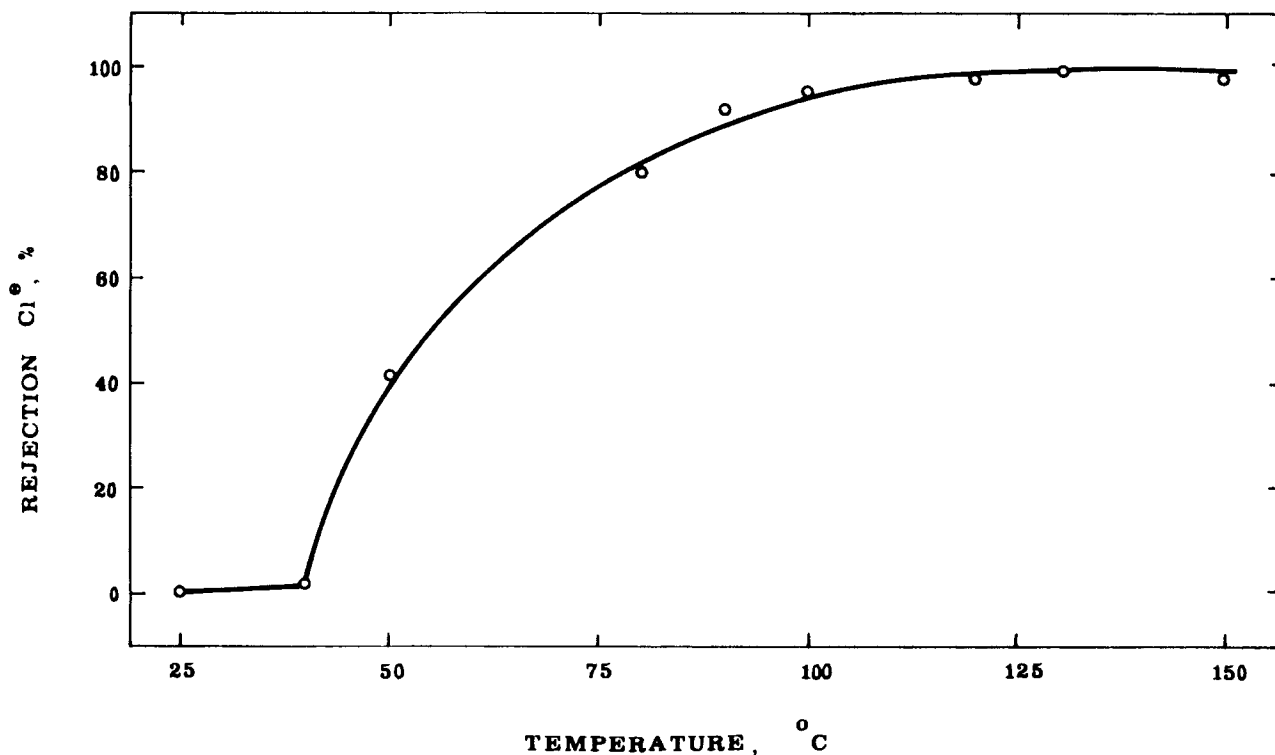


Figure 4 Effect of thermal treatment temperature on the rejection power of PTABH membranes. Values from Figure 2 obtained after 40 h of testing are taken.

and the obtained membranes were subsequently posttreated for 15 min in deionized water at 100°C.

It can be seen from these figures that while selectivity of these PTABH membranes clearly increased with increasing thermal treatment temperature, until about 130°C was reached, their permeability significantly and steadily decreased from about 60 cm³/cm² h for the not treated membranes to only 0.5 cm³/cm² h for those membranes that were heated at 130°C. However, with further increase in thermal treatment temperature, above 130°C, this trend seemed to unexpectedly change, and the membranes prepared at 150°C already showed reversion of behavior in solute rejection, which started to decrease with respect to its value determined for the membrane treated at 130°C. In addition to this, the membranes prepared at 150°C were yellow in color, in a clear contrast to those prepared at or below 130°C, which were completely colorless and transparent.

Based on these and other data reported previously for these and other similar membranes,¹⁻⁶ it seems possible to accept that this increase in membrane rejection and simultaneous decrease in permeability, which resulted from increase in thermal treatment temperature, is a consequence of overall densifica-

tion of the protomembranes, which is caused by more efficient solvent evaporation at higher temperatures. In contrast, the change of behavior at temperatures above 130°C seems to reflect some early beginnings of polymer degradation reactions that induce structural changes in the main-chain backbones of their molecules and consequently cause disruption of segmental packing organization, loosening the resulting membrane structure. In support of this suggestion, some indications of formation of oxadiazoline rings in the polymers at these temperatures have already been found by infrared analyses.⁹

Effect of Time of Exposure

Effect of the extent of thermal treatment on the membrane separation properties is shown in Figure 5 for the samples obtained by thermal treatments at 100°C. It can be seen from these data that prolongation of thermal treatment at constant temperature resulted in increase in the rejection power and simultaneous decrease in the permeant fluxes. The membranes to which the results in these figures refer were all prepared from the same polymer sample, which had \bar{M}_w of 20,350, and they were subsequently posttreated by annealing in boiling water for 1 h.

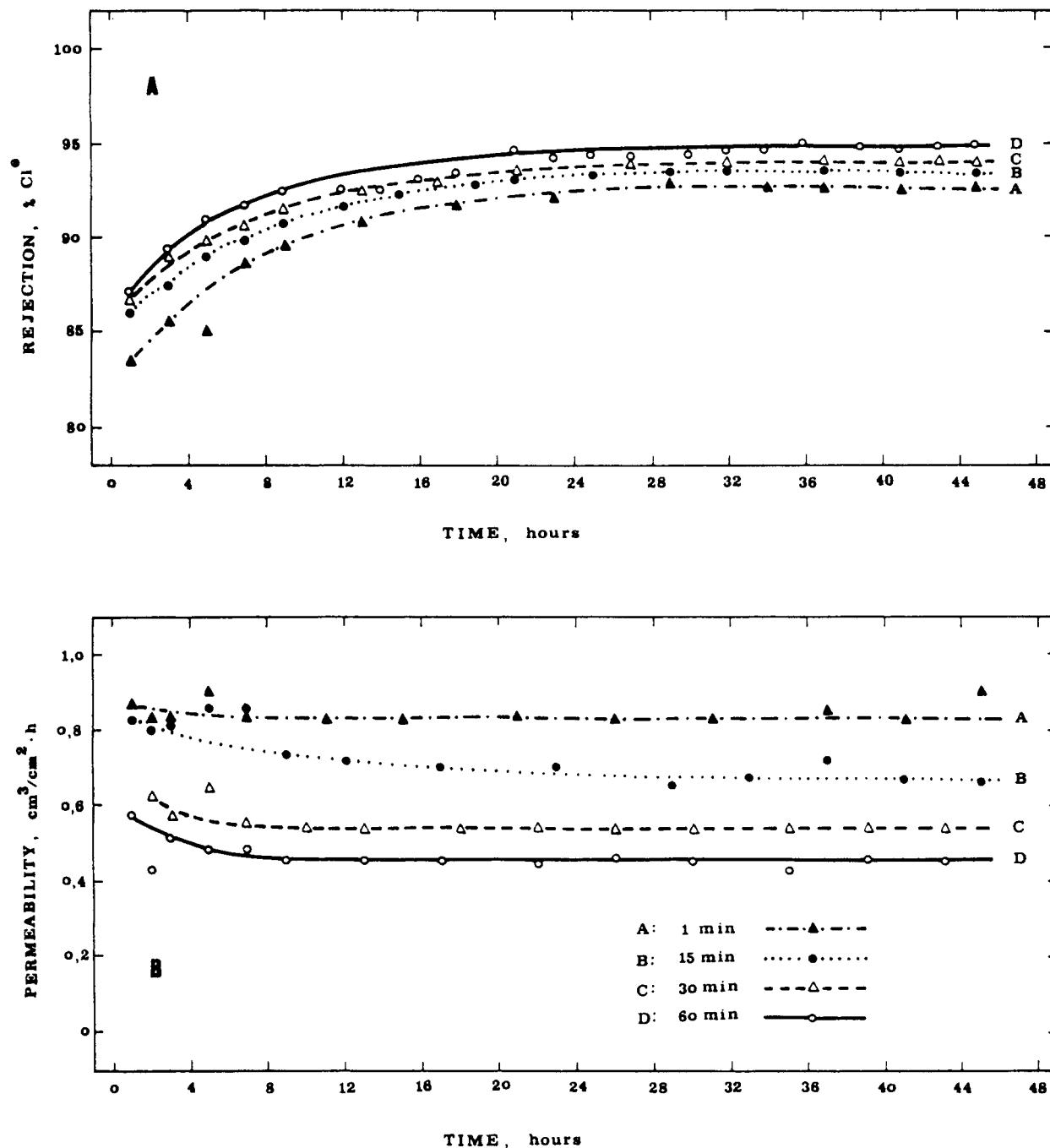


Figure 5 Separation properties of PTABH membranes as a function of the extent of thermal treatment at constant heating temperature (100°C): (A) rejection of Cl⁻ ions; (B) permeant flux. Membrane preparation conditions were as described in the text.

However, similar trends were also found in all other examined cases, so that it seems possible to conclude that such behavior appears to represent a general feature for all members of the PTABH membrane family.

Effects of Posttreatment Conditions

Effects of three different posttreatment procedures on the PTABH membrane performance characteristics were examined. These procedures involved

treatment of the coagulated membranes by annealing in deionized water at 100°C, exposure to concentrated HCl (pH = 1.42) at 25°C, and exposure to concentrated H₂SO₄ (pH = 1.42) also at 25°C.

Effects of Annealing in Boiling Water

The results obtained by annealing PTABH membranes in boiling deionized water are shown in Table I and in Figure 6. It can be seen from these data that this posttreatment procedure had clearly a very significant effect on the membrane properties, and that in all cases examined this treatment resulted in increase in the rejection power and simultaneous decrease in membrane permeability. However, it should be also noted that the magnitude of this effect was apparently inversely proportional to the selectivity that the respective membranes showed before exposure to posttreatment. Thus, while the membranes which had relatively low selectivity before annealing (below about 75–80% of Cl⁻), such as those prepared by heating at 25–80°C, showed increase in rejection power, in some cases by as much as 10–20% (as can be seen from Fig. 6 for the samples thermally treated at 50°C), for those capable of rejecting 90% or more of Cl⁻ without any post-

treatment, this improvement was considerably smaller and it usually ranged from only a few tenth of a percent to no more than several percents at best (as shown in Table I for the membranes thermally treated at 100°C).

It is interesting to note with respect to these data that annealing in boiling deionized water apparently did not require very long periods. Actually, the maximum effects were attained already after about 15 min of exposure and prolonged treatments did not result in further improvement of the membrane properties.

Effects of Exposure to Strong Mineral Acids

In contrast to annealing in boiling deionized water, exposure of PTABH membranes to strong mineral acids did not show as clear an effect on the properties of the obtained products. Thus, while, as shown in Figure 7, exposure to concentrated HCl slightly increased the selectivity of the membranes, the effect of H₂SO₄ was either nonexistent or even quite opposite. The reasons for this may not seem clear on the basis of these data only, although some polymer degradation can be expected in the latter case.

In the case of exposure to HCl, however, the resulting improvement in membrane rejection power was independent of whether the membrane had previously been annealed in boiling deionized water or not. This is illustrated by the results shown in Figure 8 for two membranes obtained from the same polymer sample and under the same preparative conditions (including annealing in boiling deionized water) except for additional exposure of one of them (A in Fig. 8) to concentrated HCl for 1 h.

Table I Effect of Annealing in Deionized Water at 100°C of PTABH Membranes Prepared by Thermal Treatment at 100°C^a

Extent of Thermal Treatment (h)	Extent of Annealing (min)	Rejection of Cl ⁻ (%)	Permeability (cm ³ /cm ² h)
2	0	97.3	0.34
	15	97.5	0.28
	60	97.7	0.28
1	0	94.3	0.75
	15	94.8	0.71
	30	94.8	0.70
	60	94.9	0.71
0.5	0	91.8	1.12
	15	92.6	0.97
	30	92.6	0.96
	60	92.6	0.95
0.25	0	85.4	2.25
	15	88.4	1.34
	30	89.0	1.23
	60	88.9	1.24

^a Testing conditions: NaCl–H₂O feed solution; concentration: 1.7×10^{-2} mol/L; pressure: 3.92×10^6 Pa; temperature: 23°C. Membranes were prepared from a 7 wt % solution of PTABH ($M_w = 20,350$) in DMA.

High-Rejection PTABH Membranes

From the preceding results, it can be clearly seen that high-rejection PTABH membranes can routinely be prepared by thermally treating thin DMA polymer solution layers at temperatures between 100 and 130°C and heating times from 15 min to 1 h. Therefore, to specify as precisely as possible the conditions required for preparation of potentially useful membranes for single-stage separation processes, the attention was focused on combined effects of these two processing variables on the properties of the obtained membranes. Some of the results obtained from this investigation are summarized in Table II.

Few interesting observations can be made from these results. First, it appears clear that for short thermal treatment times (shorter than about 15

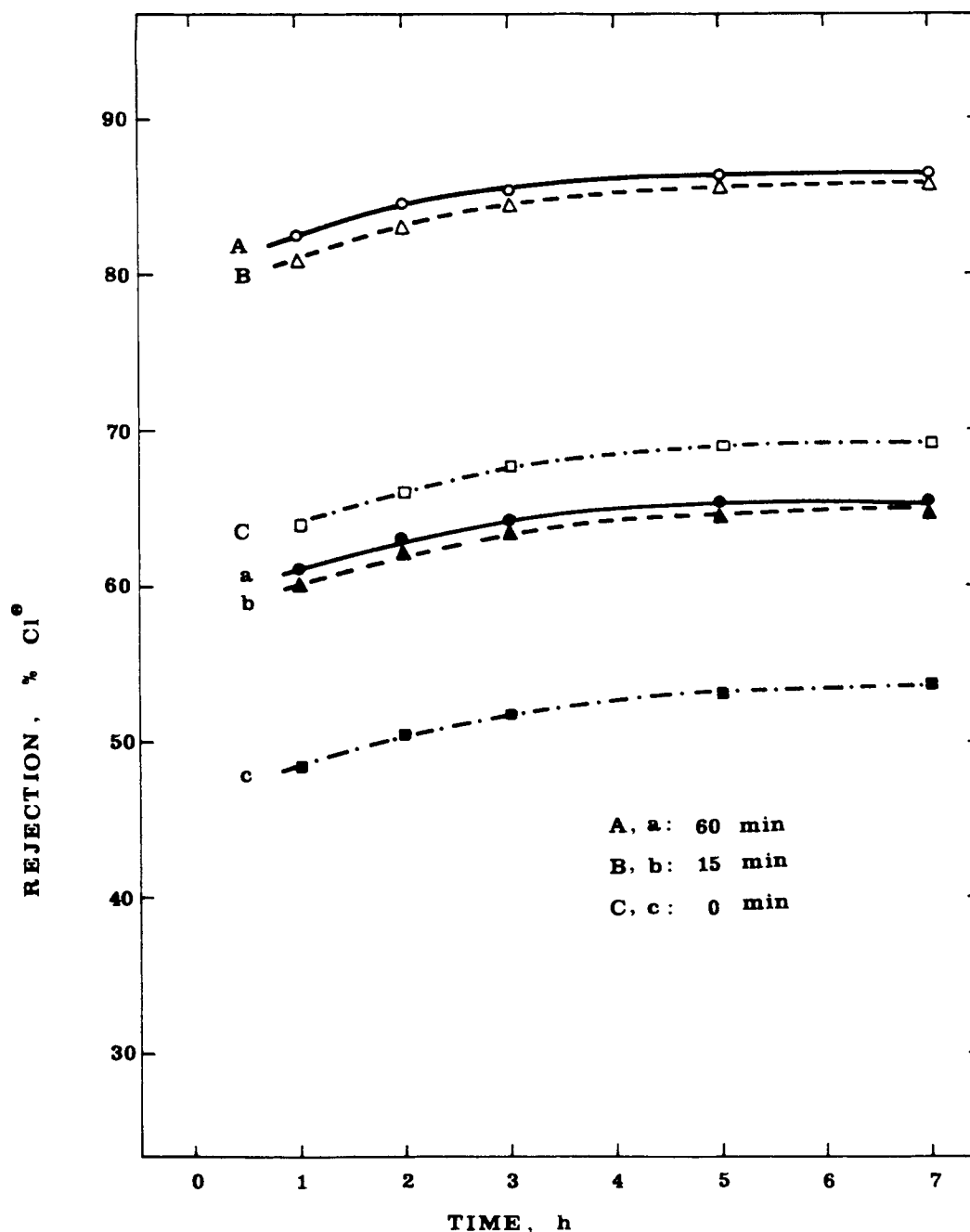


Figure 6 Effect of posttreatment annealing in deionized water at 100°C on the properties of PTABH membranes prepared from polymer samples having molecular weights \bar{M}_w of 20,350 (A, B, C) and 17,900 (a, b, c) by thermal treatment at 50°C for 5 hs.

min), selectivity of these membranes increased with temperature, so that percent rejection of Cl^- found for the sample treated at 150°C was higher than that of the sample treated at 130°C, which in turn was higher than that of the membrane treated at 100°C. In contrast to this, however, of the samples heated for either 15 or 30 min during the thermal

treatment, the highest rejections were found for the membranes exposed to 130°C, while for both heating times the samples thermally treated at 150°C showed higher rejections than those heated at 100°C. Finally, when the samples were thermally treated for as long as 60 min, it was rather difficult to clearly establish any significant difference between their

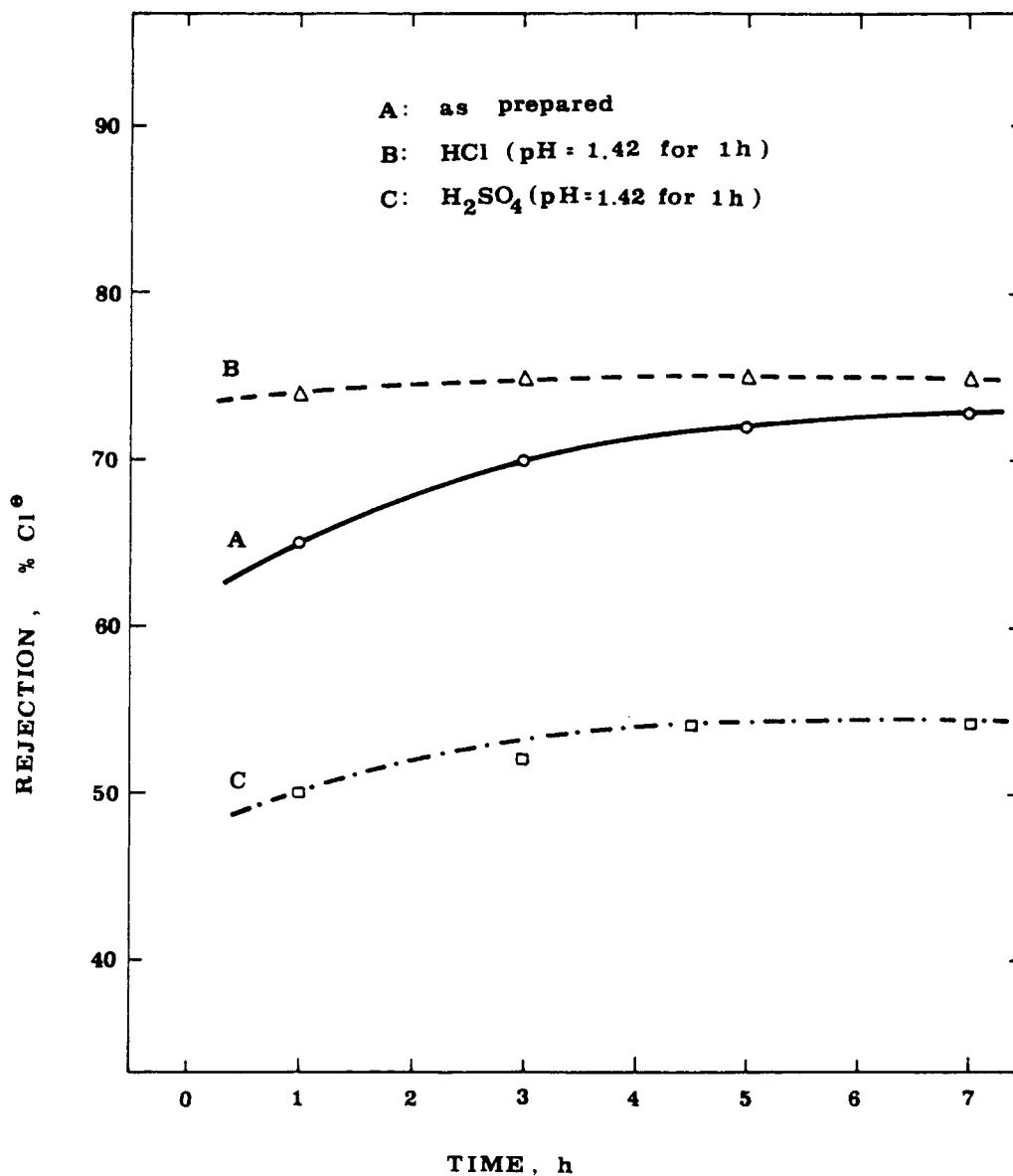


Figure 7 Effect of posttreatment exposure of PTABH membranes to concentrated strong mineral acids. Samples were prepared from a 7 wt % PTABH ($\bar{M}_w = 19,250$) solution in DMA and were thermally treated at 100°C for 30 min.

characteristics, but if there were any, then from the result obtained it appears that the lowest rejection within the series was shown by the membrane prepared at the intermediate temperature of 130°C, while the other two had practically the same selectivity, although the sample prepared at 100°C showed almost five times higher permeant flux.

These results seem to indicate possible existence of what might be termed "ceiling conditions" for thermal treatment of the PTABH membranes. If

so, these conditions would appear to represent a joint function of heating time and temperature, such that before they are reached the rejection power of the PTABH membranes increases with increase in either time of temperature, or both, but once the ceiling conditions are reached the membrane selectivity either deteriorates or remains unchanged with further increase in the values of heating parameters. This may be caused by possible irreversible changes in either polymer structure or membrane super-

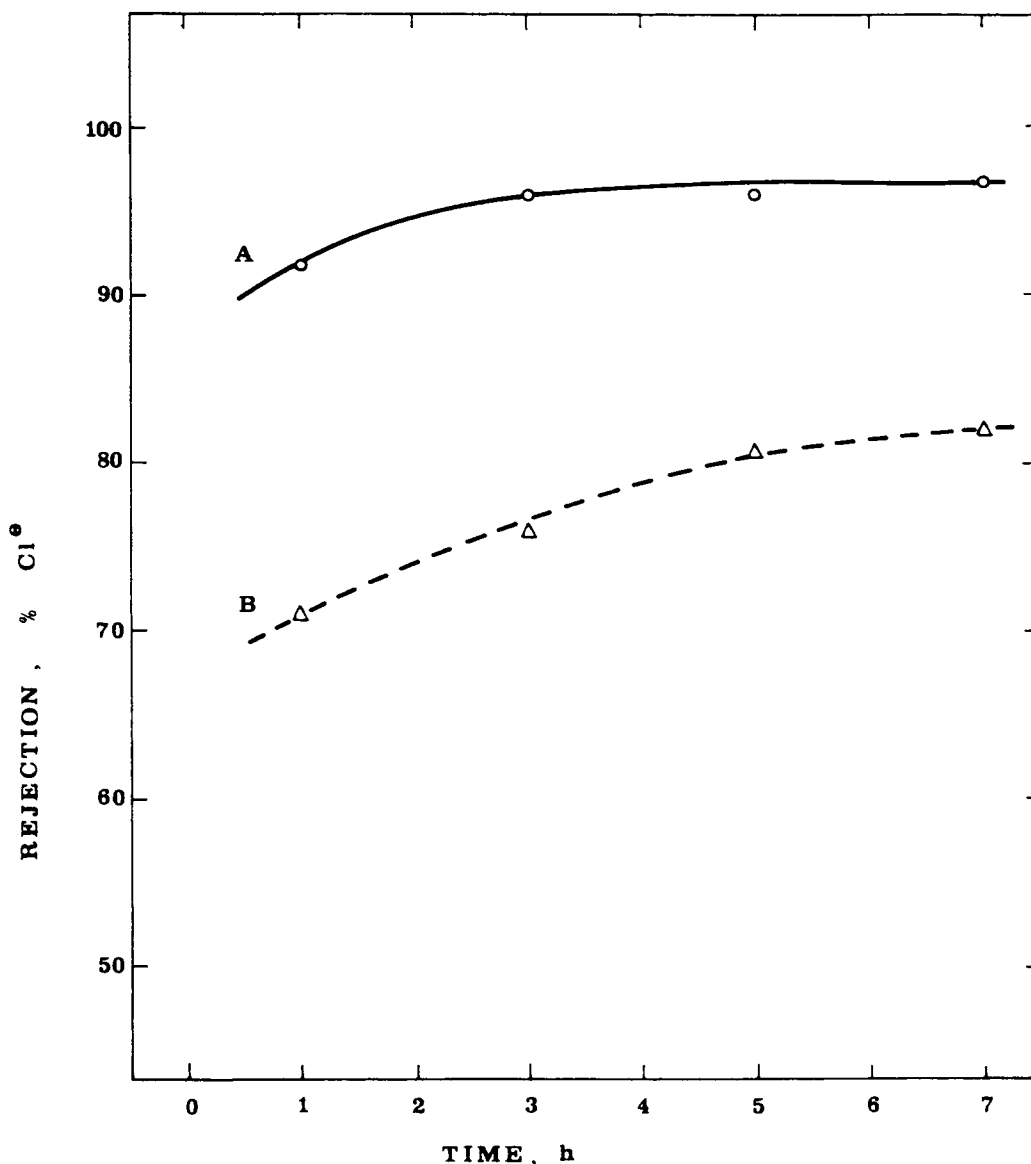


Figure 8 Effect of posttreatment exposure of PTABH membranes to concentrated HCl (pH = 1.42) after annealing in deionized water at 100°C. Samples were prepared from a 7 wt % PTABH ($\bar{M}_w = 19,250$) solution in DMA, thermally treated at 100°C for 30 min and annealed for 1 h. Sample A was exposed to acid.

molecular organization. Based on the results described herein, it seems that these ceiling conditions for PTABH membranes can tentatively be defined by the temperature of 130°C and the heating time at that temperature of about 30 min.

Of course, as discussed in the preceding section, for preparation of the membranes with rejection power of 98% or higher, application of posttreatment by annealing in boiling deionized water and/or exposure to concentrated HCl appears essential.

Effect of Polymer Molecular Weight

It is indeed interesting to note that although molecular weight and molecular weight distribution are the most important general polymer properties, which should be therefore expected to influence, at least to a certain degree, the membrane characteristics, this subject has apparently not attracted very much attention in the polymer membrane research as yet.⁴ More specifically, there has been no such

Table II Properties of High-Rejection PTABH Membranes as a Function of Time and Temperature Applied During the Thermal Treatment of Polymer Solution Layers^a

Temp. (°C)	1 min		5 min		15 min		30 min		60 min	
	<i>r</i> ^b	<i>p</i> ^c	<i>r</i>	<i>p</i>	<i>r</i>	<i>p</i>	<i>r</i>	<i>p</i>	<i>r</i>	<i>p</i>
100	88.6	0.83	86.4	1.28	89.9	0.86	90.6	0.55	93.0	0.48
130	87.4	0.68	87.2	0.08	91.4	0.18	93.6	0.19	91.2	0.49
150	91.7	0.28	93.2	0.31	91.3	0.41	92.3	0.07	92.8	0.10

^a Testing conditions were as given in Table I. Membranes were prepared from a 7 wt % solution of PTABH ($\bar{M}_w = 17,900$) in DMA and were annealed in boiling deionized water for 15 min.

^b *r* = percent rejection of Cl⁻.

^c *p* = permeability in cm³/cm² h.

investigations reported in the field of aromatic polyamide or polyamide-hydrazide membranes at all, and there seem to exist only few reports available on such investigations with other membrane forming polymers.

In this work, however, it was noted already during its early phases that considerably different performances could be obtained when membranes were prepared under identical preparative conditions but from different starting PTABH samples. For this reason it was decided to examine in more detail potential effect of the polymer molecular weight on the membrane performance characteristics, assuming for that matter that the molecular weight distribution was constant, since for all investigated samples the polydispersity coefficients, \bar{M}_w/\bar{M}_n , were found between 1.95 and 2.03.

Therefore, five different PTABH samples, having weight average molecular weights quoted in the experimental section, were prepared and used for membrane preparation. Their \bar{M}_w values were purposely selected to range from about 17,000 to about 64,500 because it has been already shown¹⁰ that viscometrically determined critical molecular weight for this polymer was about 7,000. In addition, it was also found that below \bar{M}_w of about 10,000 the membranes did not show sufficient mechanical strength to successfully withstand the working pressures applied in these testing experiments. From all five polymer samples two series of membranes were prepared by using thermal treatments at 100°C for 1 h and at 40°C for 5 h, respectively. From each of these two series three additional series were formed by annealing the parent samples in boiling deionized water for 0, 15, and 60 min, respectively. These membranes were then tested under the standard experimental conditions and the results obtained are shown in Figure 9.

It can be seen from this figure that polymer molecular weight clearly and significantly influenced the membrane separation characteristics, but also that the extent of that influence was dependent on the membrane preparation parameters in an interesting manner. Thus, while this effect was quite dramatic for the membranes treated at lower thermal treatment temperatures (40°C), it was only slight, or perhaps even nonexistent when the same was done at 100°C. Of the membranes prepared by thermal treatment at 40°C, however, those from higher molecular weight polymers showed considerably better selectivity (and consequently, also lower permeant fluxes), probably because they had smaller pores, lower pore density, and more narrow pore size distribution.

This result would seem to support the suggestion made earlier by Matsumoto and co-workers,¹¹ who proposed that relatively short polymer molecules may tend to aggregate and form small spherical micelles, causing thereby their membranes to take on an open cell structure and to allow higher permeant fluxes and lower rejection powers. Considering this from the aspect of high molecular weight polymers, it would appear that increased probability of the polymer chain entanglement, which is to be expected above the polymer critical molecular weight, should result in more tight packing of the neighboring polymer segments and, therefore, also in reduction of intersegmental free volume and in increase in degree of polymer crystallinity. In addition, in the case of relatively rigid aromatic amide or hydrazide polymers, such as PTABH discussed in this work, this should be further intensified by the pronounced tendency of these materials to establish secondary hydrogen bonding between their imino and carbonyl groups so that all these effects would then be expected to cause overall densification of the resulting

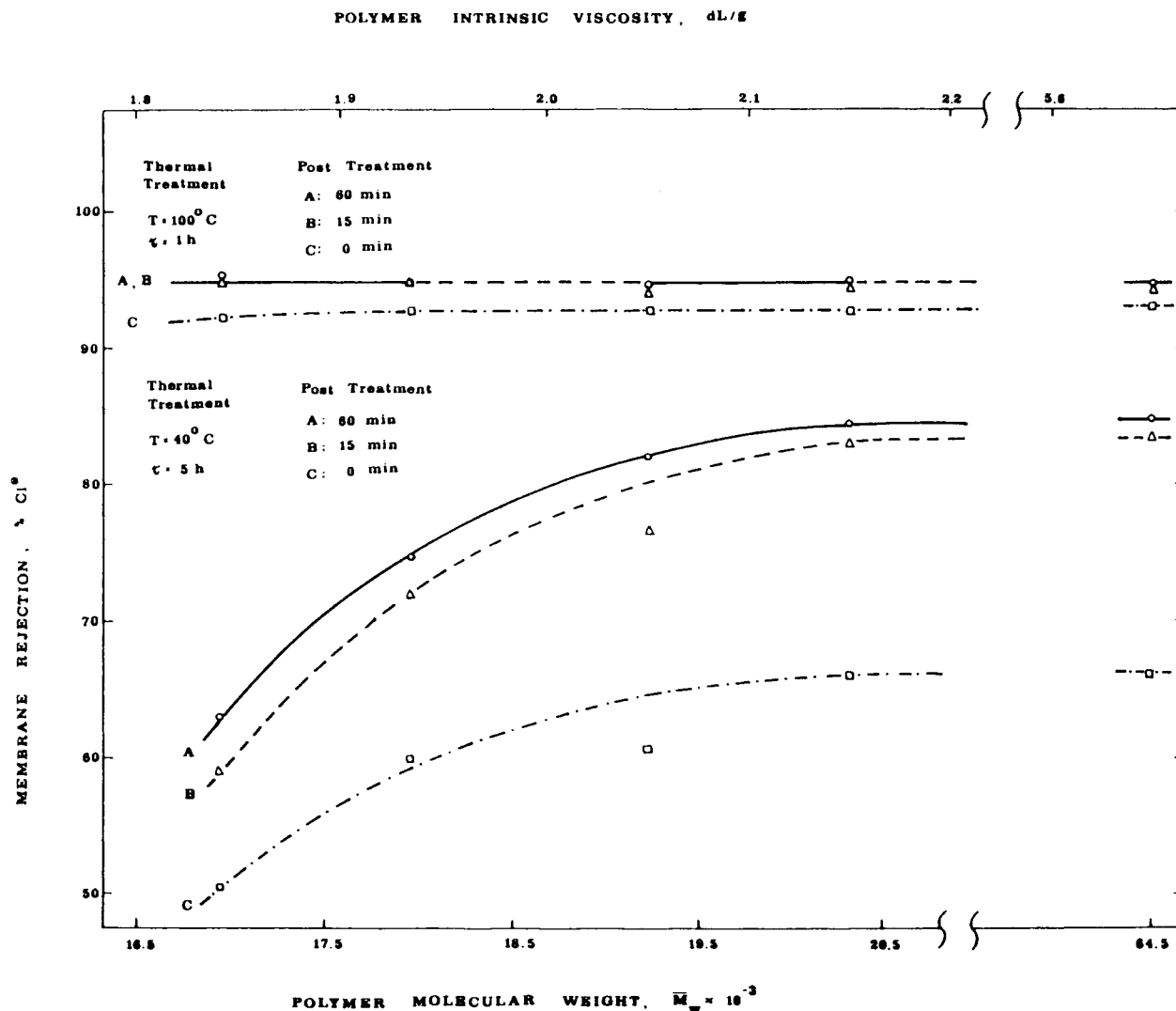


Figure 9 Effect of polymer molecular weight on rejection power of PTABH membranes. All membranes were prepared from 7 wt % polymer solutions in DMA. Other preparative conditions are given in the figure.

membranes, which should in turn show the observed higher selectivity, i.e., rejection power and porer membrane permeability.

Following this line of thought, according to the results obtained in the present work and shown in Figure 9, it seems that the critical PTABH molecular weight above which the membrane properties do not change further with the molecular weight, corresponds to about 20,000. This finding gives additional support to the results obtained earlier for the structure-property relationships for this and other closely related polymers of the aromatic polyamide-hydrazide family.⁶

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