

The Kinetics of Polyarylate Hydrolytic Embrittlement

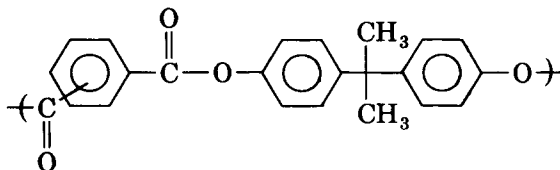
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Synopsis

The hydrolysis of polyarylate in water between 55 and 98°C was found to be a zero-order process with an activation energy of 19.2 kcal/mol, determined by changes in molecular weight. The equation for the effect of temperature on the rate of hydrolysis is $\ln k = 34.1 - 10^4/T$, where k is in day^{-1} . The decrease in molecular weight is accompanied by a loss in ductility. The transition from a ductile to brittle failure in tension occurs at \bar{M}_w of about 35,000 and \bar{M}_n of 12,700. At 27°C (80°F) and high humidity environment this would occur after 21 years. But during injection molding, the material, if not properly dried, would embrittle in a matter of seconds.

INTRODUCTION

Amorphous polyarylate is a reaction product of bisphenol A and isophthalic/terephthalic acids¹ with the repeating unit of:



The aromatic ester group in polyarylate is sensitive to hydrolysis.² The chemistry of ester hydrolysis in polyesters and in polycarbonate is well documented. Because of the similarity in chain linkages between polyarylate and polycarbonate, it has been suggested, but without supporting evidence, that the kinetics and mechanism of hydrolysis would be similar in these resins.^{2,3}

Recently, we have studied the rate of water absorption and its effect on the mechanical properties of polyarylate⁴ between 23 and 98°C. A decrease in ductility was observed and the activation energy for the hydrolytic embrittlement process was estimated to be 22 kcal/mol. This value is identical to that of polycarbonate which was calculated from the data published by Gardner and Martin.⁵ The rate of polyarylate embrittlement, however, appeared to be slower than that of polycarbonate.

We have extended that study in order to determine the kinetic parameters of polyarylate hydrolysis. The hydrolysis was followed by monitoring the decrease in molecular weight up to approximately 50%. Such a change in molecular weight is accompanied by almost total loss in mechanical proper-

ties. However, in terms of the chemistry of hydrolysis it represents the very early stage of the reaction.

EXPERIMENTAL

Molded tensile bars of polyarylate were received from Amoco. The material is known commercially as Ardel D-100. Its \bar{M}_w and \bar{M}_n are around 50,000 and 19,000, respectively. The glass transition temperature (T_g) as determined by differential scanning calorimetry (DSC), is 194°C. The tensile bars were immersed in water in stainless steel baths, which were kept at 55, 70, 85, and 98°C. The aged tensile bars which have been tested on an Instron machine, were subsequently analyzed for molecular weight and T_g .

The average molecular weights were determined by gel permeation chromatography (GPC) using a Water Associates (Milford, MA) Model 150-C ALC/GPC. The column liquid chromatograph arrangement consisted of five μ -Styragel columns in series, with permeability limits of 10, 1, 0.1, 0.05, and 0.01 μ m. The mobile phase was tetrahydrofuran (THF) (Fisher Scientific, Fair Lawn, NJ). The flow rate was 1.4 mL/min, and the column oven temperature was 30°C. The fresh and hydrolyzed samples (ca. 100 mg) were dissolved into 5 mL each of methylene chloride and the solutions were filtered through 0.5 μ m Millex-SR filters (Millipore Corp., Bedford, MA). The filtrates were diluted with the GPC solvent (2 to 1) prior to the analysis. Polystyrene standards with narrow molecular weight distribution were used for calibration.

T_g was determined by DSC using a Mettler (Princeton, NJ) model TA3000 with DSC30 measuring cell. The samples were dried in a vacuum chamber for 5 days before placing in the DSC cell. The DSC heating rate was 5°C/min.

RESULTS AND DISCUSSION

Results of weight-average molecular weight (\bar{M}_w) and molecular weight distribution (\bar{M}_w/\bar{M}_n) of hydrolyzed polyarylates at various reaction times are listed in Table I. Also included in the table are the corresponding values of the tensile elongation to break, which were obtained in a previous study.⁴ The \bar{M}_w and \bar{M}_w/\bar{M}_n of a fresh polyarylate bar are about 50,000 and 2.7, respectively. The tensile strain to break is 55–65%.

Exploratory investigation using infrared (IR) spectroscopy showed that the IR spectrum of a specimen that was aged at 85°C for 69 days ($\bar{M}_w = 20,030$) was almost identical to that of fresh polyarylate. Consequently, it was not practical to follow the limited extent of hydrolysis by the spectra. In this study the progress of hydrolysis was inferred from changes in molecular weight. It is assumed that any change in molecular weight is due only to hydrolysis.

The molecular weight distribution of the hydrolyzed samples is relatively constant and has an average value of 2.76. Since \bar{M}_n is sensitive to low molecular weight species, the above result suggests that the hydrolysis did not proceed from chain ends, but rather occurred somewhere along the polymer chain. It is assumed here that low molecular weight species would not leach out appreciably. Aqueous solutions left in the water baths were not analyzed for such species. Schilling et al.,⁶ studied the hydrolysis of bisphenol A

TABLE I
Summary of Polyarylate Hydrolysis Results

Temperature (°C)	Time (days)	\bar{M}_w^a	\bar{M}_w/\bar{M}_n	Tensile elongation (%)
55	35	49,440	2.75	55
	69	47,120	2.80	43
	108	45,760	2.77	33
	220	40,260	2.85	25
70	10	47,440	2.62	34
	35	43,710	2.71	22
	69	40,190	3.06	20
	108	35,090	2.64	12
85	5	45,920	3.05	26
	7	45,900	2.84	28
	14	42,450	2.52	20
	24	39,060	2.84	15
	35	34,010	2.67	6
	69	20,030	2.80	— ^b
98	4	43,210	2.69	27
	8	37,250	2.66	14
	11	32,970	2.68	4

^aWeight-average molecular weights by GPC relative to polystyrene standards.

^bSpecimens too fragile for testing.

polycarbonate using ^{13}C NMR (nuclear magnetic resonance) and reported that at the early stage of hydrolysis the phenyl end groups are very stable and do not represent an initiation site for rapid hydrolysis. The results obtained in the present study are also for the early stages of the reaction. The observed change in \bar{M}_w is generally less than 50%. On average, one scission per chain would bring about a 50% reduction in molecular weight.

The change in \bar{M}_w as a function of time is plotted in Figure 1. In the limited extent of reaction of this study, the decrease is linear with time, indicating a zero-order reaction with respect to \bar{M}_w . In the early stage of the process, the limiting step is the hydrolysis in the solid state which is relatively slow in comparison to the rate of water diffusion.⁴ An initial linear relationship was observed also in polycarbonate⁶ and polyester⁷ hydrolysis. The equation describing the zero-order process is:

$$(\bar{M}_w)_t = (\bar{M}_w)_0 - kt. \quad (1)$$

The rate constant, k , and $(\bar{M}_w)_0$ were calculated by least-squares analysis and are tabulated in Table II. Arrhenius plot of the rate constant, k , is shown in Figure 2. The activation energy for the hydrolysis of polyarylate is calculated to be 19.8 kcal/mol at 55–98°C. Based on embrittlement data, we have previously reported an approximate value of 22 kcal/mol.⁴ The present value of 19.8 kcal/mol for the hydrolysis reaction is in excellent agreement with the activation energy obtained for the hydrolysis of polycarbonate, which is reported to be in the range of 18–22 kcal/mol.^{5,8}

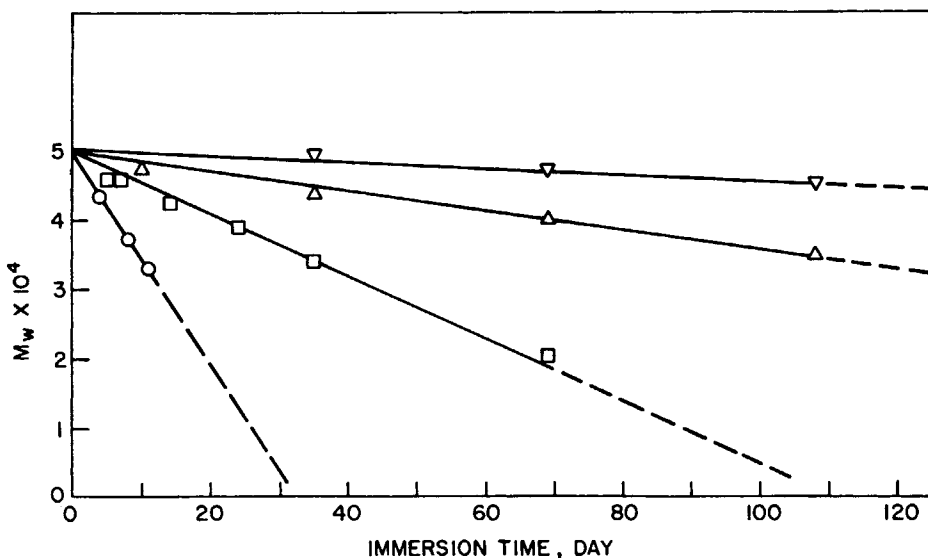


Fig. 1. Plots of \bar{M}_w vs. immersion time in water. (○) 98°C; (□) 85°C; (Δ) 70°C; (▽) 55°C.

From Figure 2 the following equation for the dependence of hydrolysis rate on temperature was also obtained:

$$\ln k = 34.1 - 10^4/T \quad (2)$$

where k is in day^{-1} and T in degrees Kelvin.

An important adverse effect of the hydrolysis is the loss in ductility of polyarylate materials and parts. The decrease in the tensile elongation to break as a function of immersion time was reported previously.⁴ We can now correlate these data with \bar{M}_w as shown in Figure 3. The elongation to break appears to be very sensitive to changes in molecular weight, as was also observed in polycarbonate⁵ and in blends of polycarbonate with polyester.⁹ The tensile yield of the polyarylate occurs at 8 to 9% strain. Unlike the strain to break, the yield strain was found to be constant as long as the material was capable of yielding. As hydrolysis proceeds and the molecular weight decreases, the material failure in tensile testing changes from ductile to brittle. For the purpose of the present discussion, the transition from ductile to brittle failure is defined as the point where the strain to break and the yield strain

TABLE II
Kinetic Parameters of Polyarylate Hydrolysis

Temperature (°C)	$(\bar{M}_w)_0$	Rate constant, k (day^{-1})
55	50,304	42
70	49,150	132
85	48,870	420
98	49,740	1545

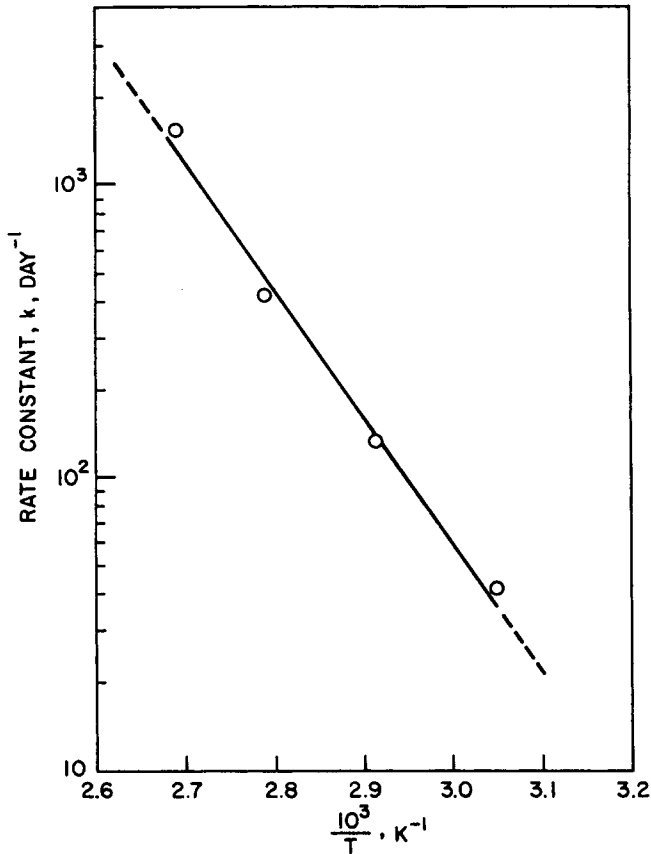


Fig. 2. Arrhenius plot of the rate constant. $E_a = 19.8$ kcal/mol.

coincide, which occurs at 8.5% strain. In terms of molecular weight, the critical value of \bar{M}_w for the transition from ductile to brittle failure in tension is about 35,000, as estimated from Figure 3. The corresponding \bar{M}_n is around 12,700. Thus, about 30% decline in molecular weight causes a drastic loss in structural properties. This is readily evident when polyarylate is injection molded. The molded parts can be quite ductile exhibiting 50–60% elongation and tensile strength of about 69 MPa. But if the resin is not properly dried before molding, the molded part may become extremely fragile. It is interesting to note that for polycarbonate the ductile–brittle transition also occurs at \bar{M}_w of about 35,000.⁵ The similarity of the two polymers' hydrolysis despite the difference of about 45°C in T_g , suggests that possibly the hydrolysis in the solid state depends mostly on water molecules concentration and mobility.

With the availability of the kinetic parameters we can estimate how long it would take for polyarylate to embrittle (i.e., a decrease in \bar{M}_w to 35,000), for example, during molding. The following calculation should be understood to be speculative because of the uncertainty in extrapolating the kinetic parameters to the high temperature of injection molding. Since data on the influence of water concentration are not available, we consider the case where sufficient water molecules are present during hydrolysis, that is, one water molecule per

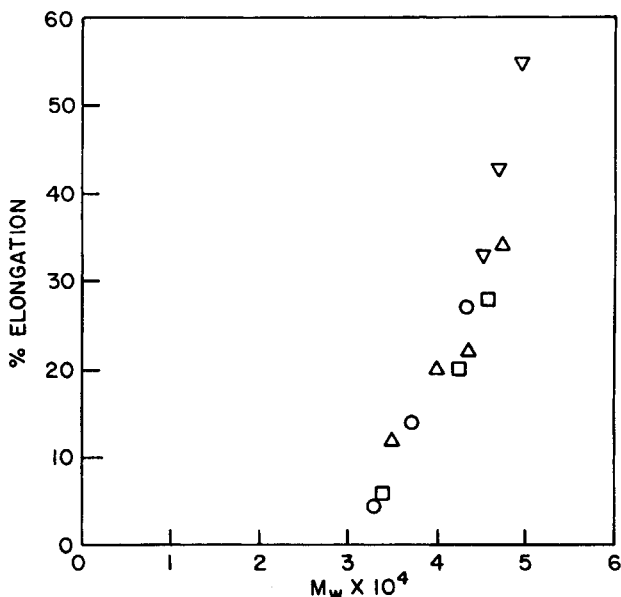


Fig. 3. The tensile elongation to break vs. \bar{M}_w . (○) 98°C; (□) 85°C; (Δ) 70°C; (▽) 55°C.

polymer chain of $\bar{M}_w = 50,000$ (ca. 360 ppm in H_2O). The manufacturer's recommended melt temperature for injection molding of polyarylate is about 365°C (689°F). At that temperature the rate constant for hydrolysis and the time for embrittlement were estimated to be about $91 \times 10^6 \text{ day}^{-1}$ and 14 s, respectively. Typically, the residence time in the injection-molding machine is of the order of a minute and, hence, it is not surprising that molded polyarylate, if not dried properly, is very fragile.

It is also possible to estimate the time to embrittlement in a typical service environment. For calculating service life of an article made of polyarylate, an average exposure temperature of 27°C (80°F) is assumed. It is also assumed that after long periods in a typical range of relative humidity of 50–75%, an equilibrium moisture content would be reached and that the rate of hydrolysis then would be dependent on temperature only. Thus, at 27°C, $k = 1.95 \text{ day}^{-1}$ and the time to hydrolytic embrittlement would be 21 years.

In addition to the decrease in mechanical properties, the decrease in molecular weight is accompanied by a decline in T_g . The dependence of T_g on molecular weight may be correlated by the well known relationship developed by Fox and Flory¹⁰:

$$T_g = T_{g\infty} - K_g/\bar{M}_n \quad (3)$$

where $T_{g\infty}$ is the T_g at infinite molecular number-average weight and K_g is an empirical constant which depends on the type of polymer^{11–14} and is usually of the order of 10^5 . The T_g data in degrees Kelvin from the hydrolyzed samples is plotted in Figure 4 according to eq. (3). These data were obtained in a DSC at a heating rate of 5°C/min. The hydrolyzed samples were dried under vacuum for 5 days prior to the DSC runs.

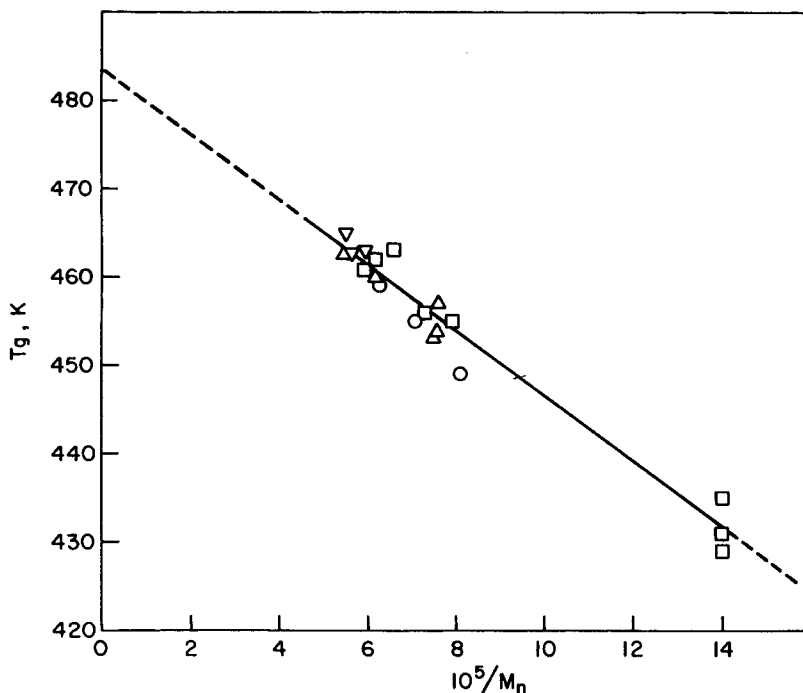


Fig. 4. The dependence of polyarylate's T_g on \bar{M}_n . (○) 98°C; (□) 85°C; (△) 70°C; (▽) 55°C.

Least-squares analysis of the data of Figure 4 gives these values: $T_{g\infty} = 483.6$ K (411°F), and $K_g = 3.75 \times 10^5$. Because the value of K_g appears to be on the high side in comparison with other polymers (for a number of polymers K_g is reported¹¹ to be between 0.5 to 2×10^5), the T_g measurements were repeated twice. Both times the samples were dried under vacuum for 5 days to avoid hydrolysis during DSC testing. The first time the drying was at 55°C and the second time at room temperature. The T_g were reproducible to $\pm 2^\circ\text{C}$ and in the majority of the measurements the same values were obtained. The data in Figure 4 are for the samples that were vacuum dried at 55°C. For the lowest \bar{M}_n (85°C, 69 days), the T_g of three different samples were measured and plotted in Figure 4. Boyer has shown that the value of K_g increases with T_g and the value obtained here for polyarylate fits reasonably well Boyer's correlation for a series of polymers.¹⁴ Fedors proposed and correlated a modified form of eq. (3) with data for various polymers.¹³ His results also show that K_g increases with T_g . An exact theoretical interpretation of the physical significance of K_g is not available. In terms of molecular parameters, Boyer has suggested the relationship of Somcynsky and Patterson¹⁵ as a guide:

$$K_g = SM_oT_g \quad (4)$$

where S is a chain stiffness factor and M_o is the segment length. It has been generally observed that T_g increases with chain stiffness. Chompff has derived a similar expression for K_g , where K_g is proportional to the effective volume of a chain end.¹⁶ In polystyrene this volume is approximately 2.3 monomer

units and $K_g \approx 1 \times 10^5$. The larger value of K_g for polyarylate may reflect the larger volume of chain ends.

CONCLUSIONS

The initial hydrolysis of polyarylate in water is a zero-order process with an activation energy of 19.2 kcal/mol. The loss in molecular weight caused by hydrolysis is accompanied by a rapid embrittlement and a decrease in T_g . Polycarbonate and some polyesters also exhibit a zero-order embrittlement process in the early stage of hydrolysis with an activation energy around 20 kcal/mol. This suggests that, at least up to one scission per chain on the average, the hydrolysis of ester and carbonate linkages in polymers in the solid state may be influenced principally by the concentration and mobility of water molecules in the polymeric matrix.

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