

Thermal Degradation of Polymers. Part XX.

The Effect of Thermal Ageing on Thermal Diffusivity and Hardness of Polyquinazolones

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Synopsis

Pre-polymers prepared from 4,4'-diaminodiphenyl-3,3'-dicarboxylic acid and aromatic diacetamido compounds have been cyclized under optimized conditions. The thermal diffusivity and hardness of these materials have been evaluated. The effect of thermal ageing on these parameters and weight loss has also been investigated. Changes in these parameters have been related to the possible structural changes occurring within these systems. These changes are discussed in terms of the potential use of these materials in tribological applications.

INTRODUCTION

In the two previous papers^{1,2} we discussed the optimization of cyclization conditions for precursor pre-polymers to yield polyquinazolones. Their structural analysis and the evaluation of thermal stability and kinetic parameters by thermal analysis was also described.

The cyclized polymers were prepared for evaluation as binder materials for poly(tetrafluorethylene), litharge and graphite which are commonly used in tribological applications in journal bearings.

Poly(quinazolones) were chosen on the basis of their reported temperature stability,^{3,4} ease of preparation, and their ability to be fabricated at the pre-polymer stage. The latter is important since it enables coatings to be formed by spraying or casting techniques on metal surfaces relatively easily and these can be converted to the more thermally stable cyclized form on heating.

In the evaluation of materials such as bearing linings the thermal conductivity and surface mechanical strength are important parameters together with the long term thermal ageing behavior as measured by weight loss. From a knowledge of the thermal conductivity or the diffusivity the rate of heat build up and the asperity temperature (surface temperature) due to frictional contact may be calculated using the Jaeger equation.⁵ In addition, Lancaster⁶ has shown hardness to be an important parameter influencing wear rate in composite bearing systems using polymer matrices.

Weight loss studies are also important when coupled with visual examination of the polymer film. Weight loss may cause destruction of the coherent nature of the polymer film by cracking or blistering, thereby increasing the wear rate.

In this paper these three parameters have been studied and the effect of thermal ageing on these parameters is discussed in terms of possible structural changes within the cyclized polymer.

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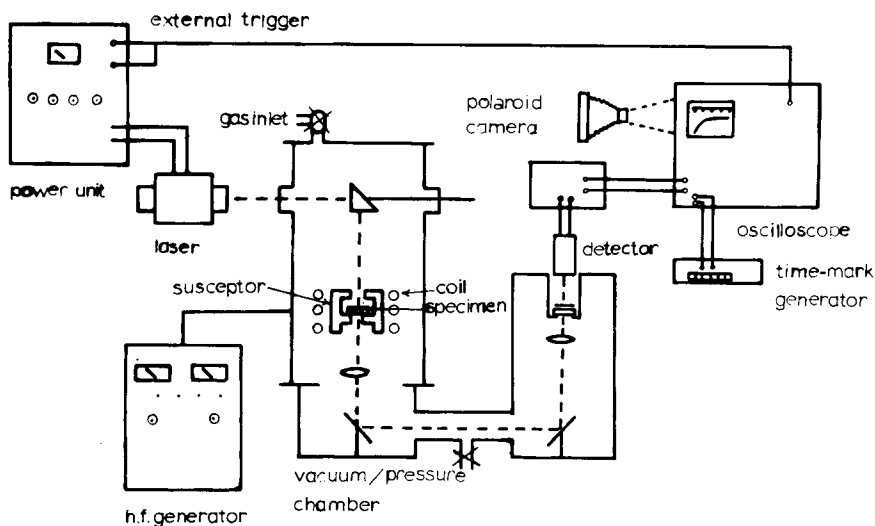


Fig. 1. Laser system for thermal diffusivity measurements.

EXPERIMENTAL

Materials

Cyclized polymers were prepared under the conditions reported previously.¹

Thermal Diffusivity Studies

The thermal diffusivity was measured for a composite specimen at 220°C using a heat pulse method and apparatus developed by Taylor⁷ based on the method originally proposed by Parker et al.⁸ The results obtained were analyzed using a computer applying a programme derived by Taylor and Bulmer.⁹

The composite samples used were prepared in the following manner. The pre-polymer sample was dissolved in the minimum quantity of distilled dimethyl formamide and this solution was cast on to a copper disk thickness 1.63 mm, diameter 6.32 mm from a small syringe. The coated copper disks were cyclized under the conditions optimized and reported previously¹ to give smooth tough polymer films which adhered strongly to the substrate.

The equipment is capable of operation between 20° and 300°C under vacuum or inert atmosphere in the pressure range 1–10 atm. A schematic diagram is

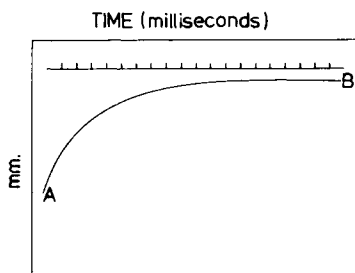


Fig. 2. Rear surface transient curve: $(B - A)/2 = t_{1/2}$.

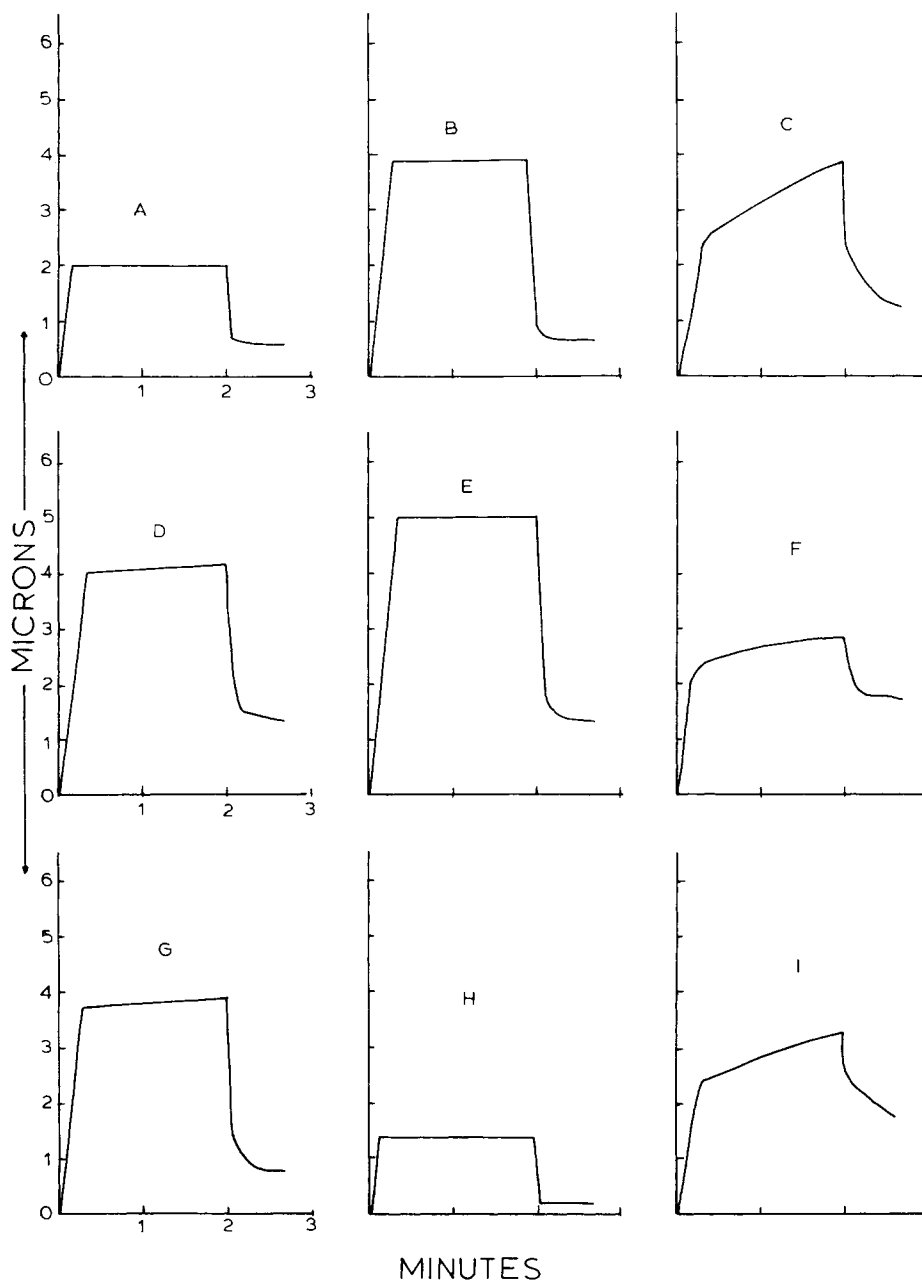


Fig. 3. Indentation-recovery curves for cyclized polymers. A = *o*-DP_c; B = *m*-DP_c; C = *p*-DP_c; D = *m*-DS_c; E = *p*-DS_c; F = DE_c; G = DM_c; H = DDS_c; I = DPY_c.

given in Figure 1. An induction coil is used to heat the sample within a graphite susceptor to the desired temperature. The heat pulse is supplied from a 100 J solid state ruby laser. The temperature transients are recorded by a lead sulphide photoconductive detector. Radiation from the sample was collected and focused using the lens and mirror system. The amplified detector output was fed to one beam of a dual-beam oscilloscope. The other beam was used to record a time comb from a time mark generator.

After the sample had attained 220°C the time marks appropriate to the oscilloscope sweep rate were set and the oscilloscope trigger was fixed at an appropriate level. The camera shutter was opened and the laser immediately triggered. When the trace was seen to clear the screen the camera shutter was closed. The rear surface temperature transient curves recorded were similar for all the cyclized polymers and a typical curve is shown in Figure 2.

Two representative polymers p -DP_c and p -DS_c were chosen to study the effect of thermal ageing in an oxidative environment on thermal conductivity. Samples were prepared as previously described, cyclized and then aged in an air oven for different time periods and the diffusivity measured.

Hardness Measurements

Hardness measurements were conducted at room temperature using an ICI Pneumatic Micro-Indentation Apparatus.¹⁰ The penetration of a (1/64) in. diameter needle into a 0.5 mm thick cyclized polymer layer deposited on a copper disk (thickness 1.63 mm, diameter 3.05 cm) was measured under a load of 16 g. After 120 sec the load was removed and the elastic recovery monitored for a further 40 sec.

Five indentation-recovery curves were obtained for each polymer specimen by applying the indenter needle to a new portion of the surface of the same specimen and the average curve obtained is shown for all specimens in Figure 3. Specimen preparation was as described for the samples used for thermal diffusivity measurements. The effect of thermal ageing in air was studied under similar conditions to those used in the thermal diffusivity studies.

Isothermal Stability by Weight Loss Studies

Long-term isothermal ageing of polymers p -DP_c and p -DS_c in air was carried out using the Stanton TR02 thermobalance in the isothermal mode. Samples (10 mg) were studied over periods up to 110 hr at temperatures in the range 250°–300°C.

TABLE I
Data Required for Evaluation of Thermal Diffusivity

Parameter	Value/units
Density of polymer ^a	1.31 g cm ⁻³
Specific heat of polymer ^b	1.50 J g ⁻¹ K ⁻¹
Density of copper	8.95 g cm ⁻³
Specific heat of copper at 220°C	40.6825 J g ⁻¹ K ⁻¹
Thickness of polymer	cm
Thickness of copper	cm
Thermal diffusivity of copper	1.0438 cm ² sec ⁻¹
Pulse time of the laser	8.0 × 10 ⁻⁴ sec
$t_{1/2}$ ^c	sec

^a Measured using a density column.

^b As reported in reference 14.

^c The time for the rear face of the specimen to reach half the maximum rise in temperature

TABLE II
Thermal Conductivities and Diffusivities of the Cyclized Polymers

Polymer Code	Thickness of polymer cm $\times 10^3$	$t_{1/2}$ ^a sec $\times 10^2$	Thermal diffusivity cm ² sec ⁻¹ $\times 10^3$	Thermal conductivity W m ⁻¹ K ⁻¹
<i>o</i> -DP _c	7.0	1.210	2.454	0.482
<i>m</i> -DP _c	8.0	1.260	3.054	0.600
<i>p</i> -DP _c	8.0	1.248	3.085	0.606
<i>p</i> -DS _c	6.5	1.240	2.051	0.403
<i>m</i> -DS _c	7.0	1.234	2.405	0.473
DE _c	8.0	1.248	3.085	0.606
DM _c	10.5	4.500	1.031	0.203
DDS _c	9.0	1.385	3.247	0.638
DPY _c	10.0	1.570	3.033	0.596

^a Measured to a precision of ± 0.25 mm giving an accuracy for $t_{1/2}$ of $\pm 2\%$.

TABLE III
Thermal Conductivities and Diffusivities of Aged Samples

Polymer code	Ageing conditions °C/hr	Thickness of polymer cm $\times 10^3$	$t_{1/2}$ sec $\times 10^2$	Thermal diffusivity cm ² sec ⁻¹ $\times 10^3$	Thermal conductivity W m ⁻¹ K ⁻¹
<i>p</i> -DP _c	RT ^a	8.0	1.248	3.085	0.606
	200/96	7.5	1.098	3.214	0.632
	225/96	8.5	1.216	3.252	0.639
	250/72	8.0	1.114	3.301	0.649
	275/48	6.5	0.904	3.548	0.697
	300/24	10.5	1.450	3.792	0.745
<i>p</i> -DS _c	RT	6.5	1.240	2.051	0.403
	200/96	8.5	1.461	2.324	0.457
	225/96	10.0	1.669	2.809	0.520
	250/72	9.5	1.547	3.226	0.633
	275/48	9.0	1.402	3.645	0.716
	300/24 ^b	7.0	1.003	3.955	0.777

^a RT = room temperature.

^b A slight degree of blistering was observed at the middle of the specimen.

DISCUSSION

Thermal Conductivity Studies

In tribological applications where only thin layers of polymer are needed and with systems such as those studied which can only be fabricated as thin film problems arise as to the method available for the measurement of thermal conductivity or diffusivity. Most steady-state methods for measuring thermal conductivity may be excluded because of the large sample thicknesses required, the very long time of measurement to reach steady-state conditions, and the problem of defining the temperature gradient across a layer of polymer. Diffusivity measurements, however, involve the evaluation of the transient time of a heat pulse through the sample. Thermal diffusivity may be measured by either periodic methods in which the thermal energy supplied to a sample is modulated and the temperature variation at various locations is compared, or by a transitory temperature method in which the sample temperature change is monitored following the input or removal of heat.

TABLE IV
 Physical Properties of Cyclized Films

Polymer code	I	E_E	E_v	η_D	$I-\eta_D$
<i>o</i> -DP _c	2.0	2.0	—	0.6	1.4
<i>m</i> -DP _c	3.9	3.9	—	1.5	2.4
<i>p</i> -DP _c	3.8	2.5	1.3	1.3	2.5
<i>p</i> -DS _c	4.2	4.0	0.2	1.4	2.8
<i>m</i> -DS _c	5.0	5.0	—	1.3	2.7
DE _c	2.8	2.0	0.8	1.7	1.1
DM _c	3.9	3.7	0.2	0.8	3.1
DDS _c	1.4	1.4	—	0.2	1.2
DPY _c	3.2	2.3	0.9	1.8	1.4

A variety of such methods have been developed.^{11,12} The one used in this study is that due to Parker⁸ which has found widespread use for single layer samples. There are, however, many environmental conditions where a layer of a second material can seriously distort heat flow to and away from a substrate. Thus Taylor⁷ has used this method to study oxide films on iron and we have adapted the method to study thin supported polymer films. Two mathematical analyses for transient heat flow through two layer solids have been reported^{9,13} and in this work the results obtained were analyzed using a computer⁹ which required the input data tabulated in Table I. The thermal diffusivities and conductivity evaluated for the cyclized polymers are shown in Table II. The results from two samples which were subjected to ageing studies are shown in Table III.

The values of thermal conductivity determined for these polymers are of the same order as those evaluated for polyamides¹⁵ ($0.433 \text{ W m}^{-1} \text{ K}^{-1}$) and polyethylene¹⁶ ($0.350 \text{ W m}^{-1} \text{ K}^{-1}$) by other methods. The thermal conductivities were different for structurally different species but due to the difficulties discussed previously¹ it is not possible to correlate the change with structure in terms of the hinge grouping. Further to this, one difficulty arises inherent in the method, namely that the different samples may have differing degrees of transparency to the laser. This will affect the amount of electromagnetic radiation absorbed by the sample which is related to transient time. This apart it would appear that incorporation of hinge groupings such as $-\text{CH}_2-$ or SO_2 cause a decrease in thermal conductivity.

The comparative results on the effect of thermal ageing in air on polymers *p*-DP_c and *p*-DS_c show that both systems increase in thermal conductivity with increasing severity of the ageing conditions. Such an observation is in accord with the observations made by Tomlinson¹⁷ on crosslinked systems and the theoretical conclusions of Yamamoto¹⁸ on the effect of increased cross linking on thermal conductivity.

It is reasonable to assume that thermal ageing will give rise to structural changes which result from crosslinking and aromatization. In such a case the Van der Waals bonding will be reduced while primary bonding will increase and polar groupings may be lost via aromatization. Such behavior would be expected to give rise to an increased thermal conductivity since the thermal conductivity through a primary bond has been reported¹⁹ to be ten times that through a Van der Waals bond. This implies that if these systems were aged at high enough temperature for long periods of time the thermal conductivity would approach that of carbon ($1.9 \text{ W m}^{-1} \text{ K}^{-1}$).

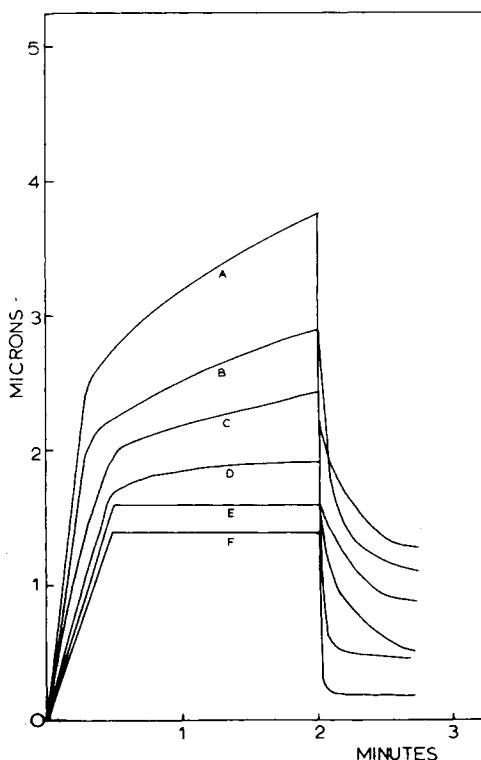


Fig. 4. Indentation-recovery curves for thermally aged samples of Polymer $p\text{-DP}_c$. (A) Original sample; (B) aged at 200°C for 96 hr; (C) aged at 225°C for 96 hr; (D) aged at 250°C for 72 hr; (E) aged at 275°C for 48 hr; (F) aged at 300°C for 24 hr.

Hardness Measurements

Hardness measurements were conducted at room temperature and the following parameters were measured from the curves obtained (Fig. 3). I , the total penetration; E_v , the viscoelastic deformation; η_D , the permanent deformation; E_E , the elastic deformation; and $I - \eta_D$, the effective indentation. The values obtained for these parameters in microns are shown in Table IV.

From Figure 3 it is apparent that coatings from polymers $p\text{-DP}_c$, DE_c , and DPY_c are viscoelastic while the rest may be classified in an intermediate category between rubbery and glassy. If the structures of these systems were ideal then it would be possible to discuss the different creep behavior in terms of the rigidity of the hinge groups and their capabilities of allowing the polymer chain to coil or uncoil when subjected to stress. However the complex structural situation does not allow such comparison although the behavior of $p\text{-DP}_c$ and $o\text{-DP}_c$ appears to be explicable in these terms. Thus in $p\text{-DP}_c$, after instantaneous bending of the bonds along the chain, the polymer chain also begins to uncoil within the time of the experiment accounting for the viscoelastic portion of the curve. Recovery might be 100% if the time scale were long enough and this applies to all curves studied. $o\text{-DP}_c$ is rigid and no uncoiling occurs due to the inherent steric hindrance of the polymer structure.

The indentation-recovery curves (Fig. 4) of the polymer $p\text{-DP}_c$ are representative of the creep behavior of the thermally aged samples at different temperatures for different times. The parameters I , E_E , E_v , and η_D were measured and are summarized in Table V together with those for $p\text{-DS}_c$ and DPY_c .

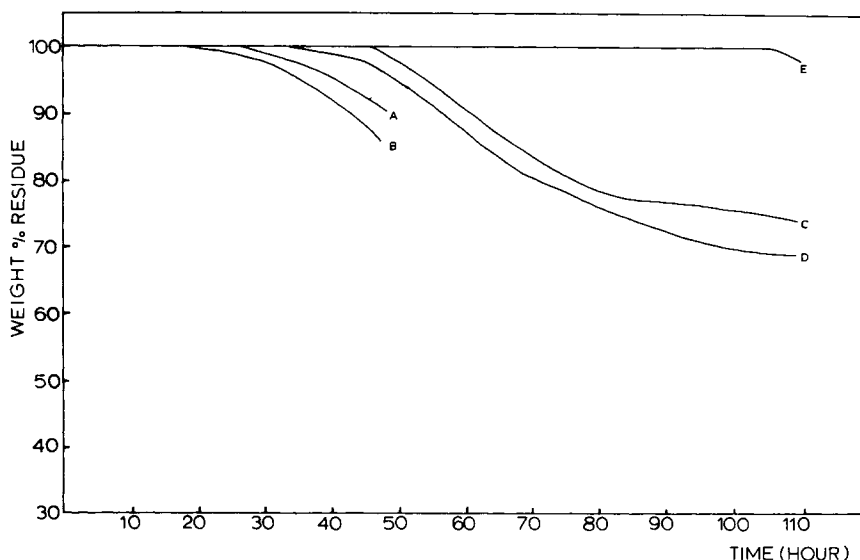


Fig. 5. Isothermal weight loss curves in air. (A) p -DP_c at 300°C; (B) p -DS_c at 300°C; (C) p -DS_c at 280°C; (D) p -DP_c at 280°C; (E) p -DP_c at 250°C.

The gradual change in shape of the indentation-recovery curve for p -DP_c (Fig. 4) suggests that on thermal ageing in air the polymer undergoes some definite chemical structure changes. This is manifested in terms of the decrease in total indentation, the reduction in viscoelastic deformation, and permanent deformation. This implies that the polymer becomes harder, the chains more rigid, and that main chain slippage is reduced to a minimum on thermal ageing. This increase in chain rigidity may arise from further cyclization or aromatization under prolonged heating and reduction in main chain slippage suggests the presence of cross links. Huffred,²⁰ in his studies on the effects of cross links and molecular weight on the creep response of amorphous polymers, has obtained similar curves to those illustrated in Figure 4, supporting this interpretation.

Attempts were made to substantiate the structural changes by spectroscopic methods but due to insolubility and the difficulties associated with dispersing the aged samples in potassium bromide, such studies were not possible. However such conclusions are in general agreement with the data discussed earlier for the effect of thermal ageing on thermal conductivity.

The weight loss curves obtained under isothermal conditions are shown in Figure 5 for p -DP_c and p -DS_c at a variety of temperatures in air. These show that changes in hardness and thermal conductivity after 20 hr are accompanied by weight loss, suggesting that concurrent oxidative degradation occurs. It is of interest however that p -DP_c is stable for 100 hr at 250°C and p -DS_c and p -DP_c are stable for 30–50 hr at 280°C with p -DS_c showing slightly inferior behavior. Furthermore it is apparent that such loss does not cause rupturing of the films, thereby making them useless for tribological applications.

It would appear that such materials would prove useful in the temperature range 200°–250°C provided their wear characteristics are suitable. It is of interest to note that "post cured" materials² are harder and more stable and could similarly find use at higher temperatures.

TABLE V
Physical Properties of Thermally Aged Cyclized Films

Polymer code	Ageing conditions °C/hr	I	E_E	E_v	η_D	$I-\eta_D$
p -DP _c	original sample	3.8	2.5	1.3	1.3	2.5
	200/96	2.8	2.1	0.8	1.1	1.8
	225/96	2.3	2.0	0.3	0.9	1.4
	250/72	1.9	1.7	0.2	0.5	1.4
	275/48	1.6	1.6	—	0.5	1.1
	300/24	1.4	1.4	—	0.2	1.2
p -DS _c	original sample	4.2	4.0	0.2	1.4	2.8
	200/96	3.5	3.5	—	1.3	2.2
	225/96	2.6	2.6	—	1.1	1.5
	250/72	2.2	2.2	—	1.0	1.2
	275/48	1.7	1.7	—	0.6	1.1
	300/24 ^a	1.4	1.4	—	0.4	1.0
DPY _c	original sample	3.2	2.3	0.9	1.8	1.4
	200/96	2.3	2.2	0.1	1.3	1.0
	225/96	1.8	1.8	—	0.6	1.2
	250/72	1.2	1.2	—	0.5	0.7
	275/48 ^b	—	—	—	—	—
	300/24 ^b	—	—	—	—	—

^a Blistering at the edge of the sample.

^b Cracking of polymer surface was observed; no measurements possible.

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