

Glass Transition in Aliphatic Polyamides

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Synopsis

The glass transition temperature is analyzed in polyamide systems characterized, owing to their chemical composition, by the absence of hydrogen bonds. The physical behavior exhibited by these systems is similar to that observed in conventional aliphatic polyamides, suggesting that, besides the hydrogen bonds, the amidic group itself plays a specific and important role in determining the polymer physical behavior generally and, in particular, the glass transition mechanism. It is surmised that this role is connected with the polar and rigid character of the amidic group, affecting chain-chain interactions and chain mobility.

INTRODUCTION

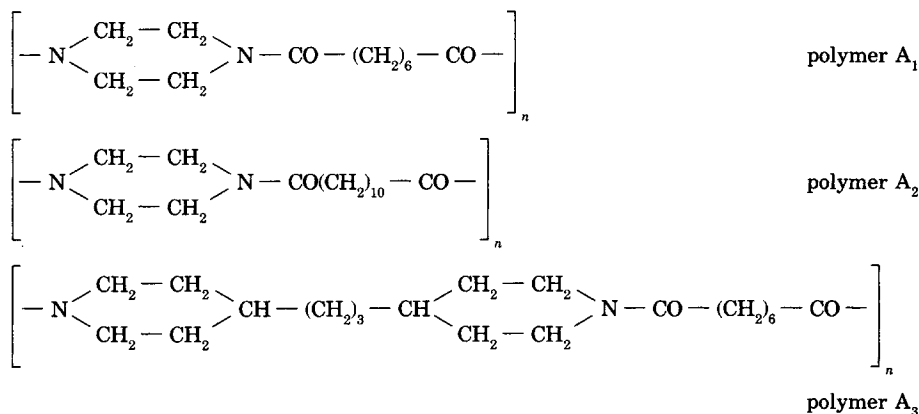
The glass-transition temperature T_g of linear polyamidic systems is considered to be markedly affected by the interchain and intrachain hydrogen bonds present in the amorphous component, such bonds behaving as a network of chemical crosslinks that reduce the chain mobility. In the model considered by Woodward and co-workers,¹ it is assumed that the main chain motions responsible for the glass-transition mechanism must involve the rupture of hydrogen bonds in the amorphous regions of the polyamides. The thermal behavior of different commercial nylons² exhibits features that are dependent on the thermal history of the sample investigated and which have been related to a glass transition temperature governed mainly by the breaking of hydrogen bonds. The fact that such features are not directly observable when mechanical testing methods were used to analyze T_g ³ does not necessarily contradict the generally accepted transition mechanism. We may accordingly expect that in polyamidic systems in which no binding hydrogen atom is contained in the amidic group the glass transition temperature must, by the accepted mechanism, be appreciably affected by the reduced molecular interactions.

With a view to obtaining additional information on the glass transition mechanism in polyamide systems in its relation to chemical features, we analyzed the physical behavior of piperazine and piperidine based aliphatic polyamides, their interest lying in that the amidic groups present in the backbone chain contain no N—H bonds available for hydrogen bonding. Some preliminary results of such analyses were reported in Ref. 4. The

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present paper reports further results obtained analyzing three different polyamides having the following repeat units:



An important consideration here is the fact that, besides the absence of hydrogen bonds, a role in determining the physical behavior of such polyamides can also be played by the piperazine and piperidine rings. In particular, specific effects like group relaxation modes and steric hindering of the chain flexibility, connected with the presence of the rings, are also expected to arise. This implies that a mere comparison with aliphatic polyamides containing hydrogen bonds is not by itself meaningful, unless at the same time the influence of the rings is duly taken into account. On the basis of such considerations (but see also the more detailed discussion below), we also prepared a polyesteric system (polymer B) containing a cyclic diol, the 1,4-cyclohexane diol, which, though different from the piperazine ring, is apt to obtaining qualitatively relevant information on the influence of hindering groups on chain flexibility and physical behavior.

The polyamidic and polyesteric polymers prepared were investigated by analyzing their thermal and viscoelastic behavior. In assessing the results obtained, particular attention was devoted to the general problem of the glass transition in polyamidic systems.

EXPERIMENTAL

Materials

Acid dichlorides were prepared by refluxing the acids with excess thionyl chloride and purified by fractional distillation. 1,4-Cyclohexane diol and piperazine were sublimated under vacuum (0.05 Torr) before use, whereas 4,4'-trimethylenedipiperidine was purified by crystallization from anhydrous toluene under a nitrogen atmosphere.

Polymer Preparation

The polymers to be investigated were obtained according to two distinct preparation procedures: Polyamides were prepared by interfacial low-temperature techniques, while the polyester was obtained by melt polycondensation. Experimental reaction conditions were similar to those adopted for analogous polymers, as reported in previous papers.^{5,6} As an example of typical low-temperature procedure, poly(piperazine suberamide) was synthesized as follows. Piperazine (0.840 g, 0.01 mol) and NaOH (0.80 g, 0.02 mol) were dissolved in 270 mL of water and placed in a 1-L blender; 2.11 g (0.01 mol) octanedioyl dichloride dissolved in 100 mL of chloroform/*n*-hexane (50/50 by volume) were quickly added while stirring. Stirring was discontinued after 10 min, and the polymer was collected on a glass filter, repeatedly washed with water, and dried under vacuum (0.1 Torr) at 50°C, the yield was 70%.

Synthesis of Poly(*cis*, *Trans*-1,4-cyclohexylene octanedioate)

1.055 g (0.005 mol) of freshly distilled octanedioyl dichloride and the corresponding stoichiometric amount (0.60 g, 0.005 mol) of (*cis*, *trans*)-1,4-cyclohexanediol were reacted in a 50-mL two-necked flask equipped with a nitrogen-gas inlet capillary. The temperature was kept at 120°C for 20 min, enough for most HCl to be liberated. The temperature was then raised to 150°C for 2 h, the occurrence of reaction being indicated by the increasing viscosity of the melt. Finally, the reaction was carried out for further 20 min at 0.01 Torr. After cooling, the polymer was dissolved in chloroform and poured in methanol. The precipitate was collected and dried under vacuum (0.1 Torr) at 40°C, giving 90% yield. Table I summarizes the polymer code, composition, and inherent viscosity, the last being indicative of molecular weight.

Measuring Techniques

The melting behaviour of the polymers prepared was investigated by a Perkin-Elmer DSC II Scanning Calorimeter. The temperature scale was

TABLE I
Inherent Viscosity Values and Chemical Composition of the Polyamides
and Polyester Prepared

Code	Carboxylic acid	Diamine	Diol	η_{inh}
A ₁	Suberic	Piperazine	—	1.33 ^a
A ₂	Dodecandioic	Piperazine	—	1.23 ^a
A ₃	Suberic	4,4'-Trimethylene dipiperidine	—	1.88 ^a
B	Suberic	—	<i>cis</i> , <i>trans</i> 1,4- Cyclohexane Diol	0.73 ^b

^a In *m*-cresol at 25°C, *c* = 0.5 g/dL.

^b In phenol/tetrachloroethane (40/60 by weight) at 30°C, *c* = 0.5 g/dL.

calibrated against high-purity standards, and the apparent enthalpy of fusion were calculated by comparing the melting endotherm of a weighted polymer sample with that of a weighted indium sample.

The viscoelastic properties were analyzed by a Tōyō Rehovibron Viscoelastometer, detecting the dynamic mechanical spectrum in monodirectional vibrational stretching over a temperature range from -100°C to a few degrees below the melting temperature. The operating frequency was 110 Hz. In addition, over the same temperature range, the linear dilatometric behavior was analyzed using a Perkin-Elmer TMS I Thermomechanical Analyzer. The dilatometric analysis yields the glass transition temperature T_g as the point where a change in the linear thermal coefficient is observed.

Both thermal and viscoelastic properties were analyzed on films obtained by die casting. In particular, the three polyamidic films were obtained by slow evaporation of concentrated formic acid solutions, while the polyesteric film was obtained from a chloroform solution.

RESULTS

Thermal Analysis

In Table II thermal data are summarized in terms of melting temperature T_m , melting enthalpy ΔH_m (as given by the DSC analyzer), and T_g as given by the dilatometric analyzer). Table II shows that polymer A₁ melts at a temperature typical of aliphatic linear polyamides, just as is typical of such polyamides its value of T_g .⁷ T_m and ΔH_m values decrease in polymers A₂ and A₃, particularly in the latter, as a consequence of the more difficult packing of the large dipiperidine groups, which gives rise to lower crystallinity. Quite a similar trend is also observed in the T_g values, which decrease in going from polymer A₁ to polymer A₃—an effect that seems reasonable to believe connected with the reduced crystallinity of polymers A₂ and A₃. It is in fact known that the crystalline content affects the T_g value, both generally⁸ and, in particular, in polyamide systems.⁹ The dependence of T_g on crystallinity prevents us from considering here the results obtained on *N*-substituted aliphatic polyamides.¹⁰ In these systems, in fact, in the ab-

TABLE II
Thermal Data of Piperazine and Dipiperidine-Based Polyamides (A Series) and 1,4-Cyclohexane Diol-Based Polyester (B Polymer)

Polymer	T_m ($^{\circ}\text{C}$) ^a	ΔH_m (J/g) ^a	T_g ($^{\circ}\text{C}$)
A ₁	242	41.6	90
A ₂	150	25.9	79
A ₃	124	15.4	61
B	157	36.8	-20

^a The values of T_m and ΔH_m have an estimated reproducibility of $\pm 0.5^{\circ}\text{C}$ and ± 2 J/g, respectively.

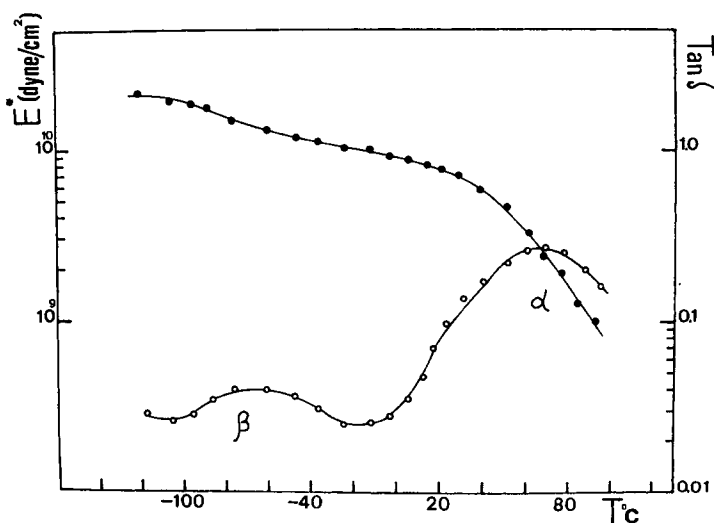


Fig. 1. Viscoelastic spectrum of sample A₃.

sence of hydrogen bonds, the observed T_g values were below 0°C, but the crystallinity content was practically zero. As to polymer B, its T_g value lies in a range that is typical of the linear polyester systems⁷ and is markedly lower than those of polymers of the A series.

Viscoelastic Behavior

The dynamic mechanical spectra are characterized by two main dissipation bands. As an example of the general trend observed in the three polyamides and the polyester polymer, Figure 1 shows the spectrum detected in the case of polymer A₃. From the viscoelastic spectra, two transition temperatures can be defined, namely, the temperatures where the two relative maxima can be defined, denoted by α and β , respectively, the higher- and lower-temperature transition, the values of T_α and T_β observed are summarized in Table III.

Comparing the T_α and T_g values of the same polymers (Tables II and III,

TABLE III
Viscoelastic Data of the Polymers Prepared and Investigated

Polymer	T_α (°C)	T_β (°C)
A ₁	130	-85
A ₂	90	-87
A ₃	72	-70
B	-3	-55

respectively), and considering that a shift to higher temperatures is to be expected in replacing the thermal method by a dynamic mechanical analysis,¹¹ we may identify the α -transition with the glass transition. Further support for such an identification is provided by the significant decrease of the complex modulus observed at T_α in the viscoelastic spectra. As to the lower temperature, the β -transition, we may assume it to be related to ring-relaxation modes. For polymer B, this assumption is supported by literature data¹² concerning dielectric and mechanical relaxations in polymers that contain the cyclohexyl unit. In fact, a transition at -55°C (110 Hz) is in agreement with the data reported in the literature, and it can be ascribed to the conformational transitions between the two forms, typical of the cyclohexyl ring. Based on the above, it may be surmised that in the polyamidic polymers the β -transition is connected with a similar mechanism involving the ring of such polyamides.

In addition to the mere comparison with the cyclohexyl case, further support for the hypothesis is provided by the following two considerations. In the first place, the T_β transition temperature has practically the same value in polymers A_1 and A_2 , i.e., in polymers that contain the same ring unit in a very similar steric neighbourhood, while it is shifted to a substantially higher value in polymer A_3 , which contains a more sterically hindered bicyclic unit. In the second place, the frequency dependence of the T_β transition temperature gives an approximate activation energy for the transition process that can be reckoned to be consistent with the ring conformational transitions.¹³ It is also noteworthy that in conventional polyamides a β -transition is present at about -40°C ⁸ and is considered to be connected with water/amidic group interaction phenomena.

In the piperazine system such a transition, even if present, could be masked by the observed dissipation band which is broad enough to cover a larger temperature range.

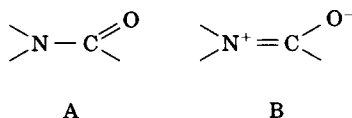
DISCUSSION

The results obtained on the glass transition temperature indicate that in the investigated polyamides the transition falls in a temperature range that is typical of the aliphatic polyamides. On this basis, one could conclude that the absence of hydrogen bonds does not shift in a significant way the transition to a lower temperature range. However, a conclusion reported in such simple terms does not take into account important elements that can affect the observed behavior. The first element is the presence of the piperazine ring that can increase the chain stiffness and therefore can increase the temperature of the main transitions, i.e., T_m and T_g . In particular, the lower ΔS_m due to a possible persistent rigidity of the chain in the amorphous phase could determine a T_m increase. The data reported in Table II suggest that this is not the case because the higher observed temperature, i.e., 242°C in A_1 sample, is practically that normally observed in flexible systems like the polyadipamide. This evidence is not completely surprising owing to a not negligible conformational mobility in the piperazine ring, if compared to aromatic cycles, that affect in a considerable way the T_m values (e.g., in

the case of the polyphenyladipamide T_m is about 400°C). Anyway, a possible effect connected to the presence of the ring, in particular on T_g value, cannot be excluded, and the comparison between samples A and B, even if in qualitative way, can give some contribution on this point. The above-reported results show that the ring does not increase appreciably the T_g value of the polyester B. Even if we underline that the conformational mobility in the cyclohexane ring is higher than in the piperazinic one and that the oxygen atoms that link the cycle to the chain give a contribution to the overall chain flexibility; however, the observed T_g indicate that a paraffinic cycle, characterized by an appreciable conformational mobility, does not increase the chain rigidity in such way to affect in relevant way the main transition and in particular T_g . On this basis, we do not expect dramatic effects connected to the stiffness of the piperazine ring.

Similar trend has been observed in the case of T_β values; as matter of fact, if it is correct to assume T_β related to the ring conformational transitions, then the observed T_β values indicate that the conformational mobility in the piperazine and cyclohexane rings are not different in a significant way. The second element that is important to point out is the correlation between T_m and T_g that, in general, are ruled by the empirical relation: $T_m \cong \frac{3}{2} T_g$ (K). Of course, this relation is very approximate; but if we want to consider it, we find that polymer B shows a T_m that is larger than in polymers A₂ and A₃, but a T_g that is about 80°C lower. In a parallel way, T_m decreases going from sample A₁ to sample A₃, but T_g decreases slower than the expected on the basis of the relation $T_m \cong \frac{3}{2} T_g$, that gives 70°C, 9°C, and -8°C for the samples A₁, A₂, and A₃ respectively.

On the basis of all the previous considerations we suggest that a specific role is played by the amidic group itself, without denying the role of the hydrogen bonds, when present, on the glass transition mechanism in aliphatic polyamides. The specific role of the amidic group can be related to specific steric and electronic features. The electronic structure of the amidic group is generally assumed to be a resonance hybrid between the following two forms¹⁴:



implying that the π electrons of the C=O double bond give to the N—C bond a partial double bond character which quantified by a rotational barrier of 18 kcal/mol.¹⁵ There follow both partial rigidity of the group and polarization between the nitrogen and oxygen atoms, i.e., features that can both affect the glass transition temperature, connected as it is with the activation of conformational motions of long sequences of the backbone chain. The rigidity of the N—C bond suggests that from this point of view

the influence of the amide group may be assumed to be not too different and anyway not larger than that of a carbon-carbon double bond. The influence of carbon-carbon unsaturation on the glass transition temperature of polyamidic and polyesteric systems had been previously investigated.^{16,17} It had been found that such an influence was negligible in polyamides, while in polyesteric systems a slight increase of T_g with increasing unsaturation content was observed. This suggests that a more important role must be played by the polar character of the amide group, which markedly enhances the cohesive intermolecular energy, thereby reducing the chain mobility and raising the glass transition temperature. We may accordingly conceive the amorphous phase of a polyamide as a network of dipole-dipole interactions in which a network of hydrogen bonds may be superimposed. The energy cost of a hydrogen-bond rupture is in the range 2-10 kcal/mol,¹³ while the rotational barrier for the N-C bond is 18 kcal/mol.¹⁴ This means that it is easier to break a hydrogen bond than to activate the free rotation around the N-C bond with consequent destruction of the bond polarity. In other words, the governing mechanism of the glass transition may well be the destruction of dipolar interactions rather than the breaking of hydrogen bonds. Even if this hypothesis seems supported by the experimental results here reported, though, no doubt, a more extensive analysis of different chemical structure within the class of aliphatic polyamides is required. In particular, we cannot totally exclude that some specific combination of effects like dense packing, molecular stiffness, and others is responsible in the piperazine and piperidine samples of the high T_g values even in the absence of hydrogen bonds.

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