Structure and Properties of 6/6.9 Copolyamide Series. I. Amorphous Phase

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SYNOPSIS

The amorphous phase of a series of random 6/6.9 copolyamides was investigated. It was characterized by the glass transition temperature (T_g) and the hydrogen bond content, as a function of the copolymer composition, compared to the corresponding homopolymers, polyamide 6 and polyamide 6.9. The hydrogen bonds in the amorphous phase have a major influence on the copolymer properties. The glass transition temperature decreases as either comonomer content increases, attaining a minimum value at about 1 : 1 molar composition. This is due to the decreased content of hydrogen bonds, their broader strength distribution, and the decreased degree of crystallinity. In addition to the usual effects, quenching in the present system causes the formation of a less dense and less regular hydrogen bonds network, reducing the T_g. Following room temperature aging, the usual hydrogen bond content is restored. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The amorphous phase of a polymer is characterized by its glass transition temperature T_g that is determined by such factors as chain structure and conformation, intermolecular interactions, the efficiency of molecular packing in the amorphous state, and by the relative amount of the crystalline phase. The T_g of polyamides is also greatly affected by hydrogen bonding. Miyake[1] and Trifan and Terenzi[2] concluded that at room temperature most of the amide groups in polyamides are hydrogen bonded, irrespective of the number of CH_2 groups in the chain. As the amide group concentration increases, the hydrogen bond density is higher, and the segmental mobility is more restricted, resulting in a higher T_g.[3]

Introduction of a comonomer into a polymer by random copolymerization interferes with the intermolecular interactions and results in modification of its properties. The effect of composition on the T_g of several series of aliphatic random copolyamides, copolyamide-6/12 and copolyamide-8/12, was studied.[3–5] It was reported that the incorporation of

a comonomer (different lactam) into a polyamide reduces its T_g, and the T_g vs. composition curve exhibits a minimum at an equimolar composition. These results do not fit the theorem of Fox[6] for random copolymers that predicts a monotonic decrease in T_g with composition, with the copolymer T_g being between the T_g values of the corresponding homopolymers without the presence of a minimum. It was suggested that such behavior is due to a reduced regularity of the amide groups distribution along the polymer chain. Hatakeyama and Kanetsuna[7] investigated several compositions of random 6/6.6/6.10 terpolyamides by IR spectroscopy and concluded that the terpolyamides exhibit lower T_g than their corresponding homopolyamides due to a higher content of unbonded amide groups. Similar results were obtained by Schroeder and Cooper[8] for 6/8/11 and 6/8/12 terpolyamides. In contrast with this conclusion, Kehayoglou[9] found that IR spectra of the 6/12 copolyamide series indicate substantially complete hydrogen bonding of amide groups over the whole range of composition, so that distortion of segments must have occurred to bring all amide groups into bonding positions.

In the present study a series of random semicrystalline 6/6.9 copolyamides was investigated to better understand its amorphous structure, as a function of composition. In addition to their com-

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mercial interest, this series studies the behavior of the copolymers' amorphous phase containing strongly interacting comonomers. Differential scanning calorimetry (DSC) was used to study the T_g behavior and FTIR spectroscopy was used to evaluate the hydrogen bond content. In addition, the degree of crystallinity was determined by X-ray diffraction, to study the effect of the crystalline phase on the behavior of the amorphous phase. An attempt was made to quantitatively correlate the T_g values with the hydrogen bonds content.

EXPERIMENTAL

Materials

In the present study a series of random 6/6.9 copolyamides (poly [HN — (CH$_2$)$_5$ — CO]-co-[HN — (CH$_2$)$_6$ — NH — CO — (CH$_2$)$_7$ — CO]), provided by EMS laboratories (Switzerland) was investigated. The 6/6.9 monomer weight ratios in the series were: 100/0, 80/20, 63/37, 51/49, 44/56, 30/70, 10/90, and 0/100.

Random copolymers were obtained through the copolymerization of the following monomers: azelaic acid, HOOC — (CH$_2$)$_7$ — COOH; hexamethylene diamine, H$_2$N — (CH$_2$)$_6$ — NH$_2$; ω-aminocaproic acid, H$_2$N — (CH$_2$)$_5$ — COOH. The acidic groups in the azelaic acid and in the ω-aminocaproic acid have the same reactivity and the amino groups in the hexamethylene diamine and in the ω-aminocaproic acid also have the same reactivity. Therefore, it can be assumed that the copolyamides are completely random.

Thermal Analysis

The glass transition temperature was determined by differential thermal analysis using an indium calibrated Mettler TC 10 A differential scanning calorimeter. The measurements were carried out on samples of 10 mg under N$_2$ atmosphere. The samples were heated from −20° to 250°C (above their melting points), cooled to −20°C, and reheated, all at a rate of 10°C/min. The second heating run was used to determine the glass transition temperature. To maximize the amorphous content, samples were heated on a plate above their melting point, quenched by liquid N$_2$, and then heated in the DSC cell at a rate of 10°C/min, yielding the T_g of the quenched polymer ($T_{g\text{quenched}}$).

FTIR Spectroscopy

Hydrogen bond content was determined by FTIR spectroscopy as a function of composition and thermal history. Thin films (10–20 μm) were prepared by casting 0.5% solutions of polymer in formic acid into petri dishes. After solvent evaporation at 100°C, the samples were vacuum dried for 12 h to remove residual solvent and water, and then stored in a dessicator until testing in the spectrometer. A Mattson 1000 FTIR spectrometer was used in the range of 400–4000 cm^{-1}, at a 2-cm^{-1} resolution. To investigate changes of the spectrum with time, films were quenched in liquid N$_2$, held at room temperature for various times (2, 5, 10, and 20 min), and then examined by FTIR.

The NH stretching region typical of polyamides, which spans a 3000–3650 cm^{-1} range, was used for the determination of hydrogen bond content. This region comprises three main bands[10–13]:

1. a sharp narrow band at 3300 cm^{-1}, attributed to hydrogen bonded NH groups;
2. a wide and weak band at 3450 cm^{-1}, attributed to "unbonded" NH groups;
3. a shoulder at 3200 cm^{-1}, attributed to two phonon vibrations involving the intense carbonyl vibrations in Fermi resonance with the NH stretching fundamental vibration;
4. a weak band at 3080 cm^{-1}, presumably obtained when neighboring amide groups both give rise to a hydrogen bond.

To evaluate the relative content of hydrogen bonded amide groups the NH stretching rather than the amide I region was selected. The NH stretching is an essentially isolated vibration and the amide I is comprised of several different contributions. The percentage of hydrogen bonded amide groups was calculated according to the Bessler and Bier method[14] that assumes that the amount of both "free" and "bonded" NH groups is proportional to the peaks' absorption. As shown in Figure 1(a), a straight baseline from 3000 to 3650 cm^{-1} was used and the intensities at 3300 and 3450 cm^{-1} were calculated by the Fourier IR software. The Bessler and Bier equation is as follows[14]:

$$\%NH(\text{bonded}) = \left[1 - \frac{I(\text{free})}{I(\text{bonded}) * \dfrac{\varepsilon(\text{free})}{\varepsilon(\text{bonded})} + I(\text{free})} \right] \times 100 \quad (1)$$
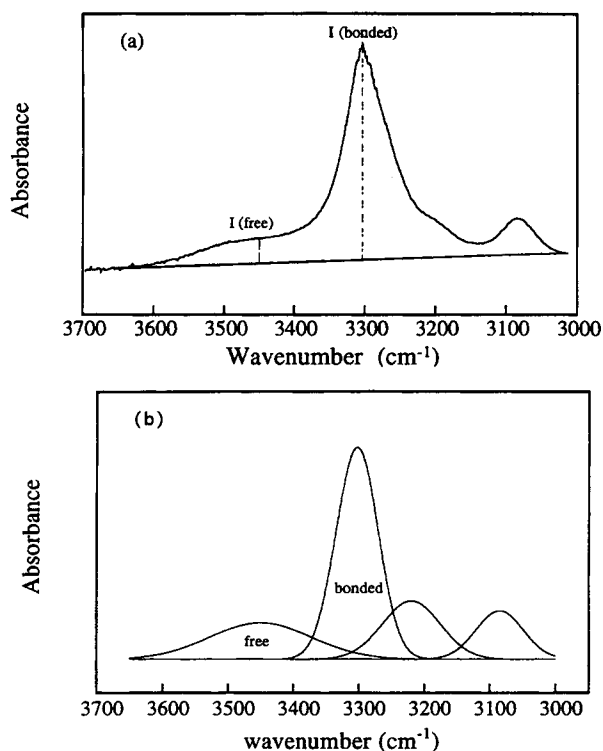
Figure 1 Determination of fraction of hydrogen bonded amide groups by the (a) Bessler and Bier[14] method and (b) "profile fitting" method (the fitted curves are shown).

where $I(\text{free}) = I(3450)$ is the absorption intensity of free amide groups, $I(\text{bonded}) = I(3300)$ is the absorption intensity of hydrogen bonded amide groups, and a factor $\varepsilon(\text{free})/\varepsilon(\text{bonded}) = 1/1.6 = 0.625$ is applied to correct for the differences between the absorptivity coefficients of the free and hydrogen bonded NH groups; ε is the extinction coefficient of Beer's law, $I/I_0 = \exp(-\varepsilon c l)$.

The FWHM (full width at half maximum) of the hydrogen bonded NH groups' band (at 3300 cm^{-1}) was calculated as well. This parameter is affected by the hydrogen bonds' strength distribution.

Another method for evaluation of hydrogen bond content, which resembles the method of Skrovanek et al.,[12,15,16] was applied. This method, called in this study "the profile fitting method," is based on curve fitting in the NH stretching region. A straight baseline was chosen from 2500 to 3650 cm^{-1} and the NH stretching region was resolved into four Gaussian bands (at 3300, 3450, 3200, and 3080 cm^{-1}) as shown in Figure 1(b). The percentage of hydrogen bonded amide groups was calculated by applying eq. (1), using the maximal intensities of the fitted curves. A third estimation of hydrogen bond content was based on the areas under the fitted curves rather than just peak intensities.

Two different values for the correction factor in eq. (1), $\varepsilon(\text{free})/\varepsilon(\text{bonded})$, are found in the literature. Bessler and Bier[14] used the ratio 1 : 1.6 suggested by Jones[17] who had investigated numerous aliphatic monomers containing amide groups. Skrovanek et al.[12] used the ratio 1 : 3.2 suggested by Macknight and Yang[18] who had investigated three series of polyurethanes. The hydrogen bond content in the present work was calculated considering the above two values of the correction factor.

X-Ray Diffraction

Wide angle X-ray diffraction was carried out to determine the degree of crystallinity by a Philips PW 1820 X-ray diffractometer, using filtered Cu-Kα radiation ($\lambda = 1.54$ Å). The diffractometer was operated at 40 kV and 40 mA. Samples of 15 × 10 × 2 mm in size were prepared by melt pressing following by slow cooling to room temperature. The diffraction patterns were obtained by scanning the interval of $2\theta = 5 \rightarrow 50°$C, at a rate of 0.01°C/s. An amorphous standard was prepared by placing a 6/6.9 copolymer sample of 44/56 composition on a hot plate, maintained at approximately 30°C above the copolymer melting point for 15 min, followed by quenching in liquid N$_2$, where it was kept just until the analysis was done. APD (automatic powder diffraction) 1700 software was applied for profile fitting, which enabled estimation of percent crystallinity.

RESULTS AND DISCUSSION

Glass Transition Temperature

The glass transition temperatures of the 6/6.9 copolyamides as a function of comonomer 6.9 content after cooling from the melt at 10°C/min is depicted in Figure 2. The onset, the middle, and the end temperatures of the transition are presented. The observed T_g values of polyamide 6 and polyamide 6.9 (52° and 43.5°C, respectively) are similar to those found in the literature: 49° and 45°C, respectively.[19,20] The T_g value of polyamide 6 is higher than that of polyamide 6.9 due to the higher amide groups concentration, that is 14.5 compared to 12 CONH/100 chain atoms, resulting in a higher hydrogen bond concentration. Although the T_g values of polyamides 6 and 6.9 are quite close, the T_g vs. composition curve has a distinct U shape; the T_g of all the 6/6.9 copolyamides studied is lower than that of either homopolyamide. The minimum T_g value was obtained for the composition of approximately equal weight
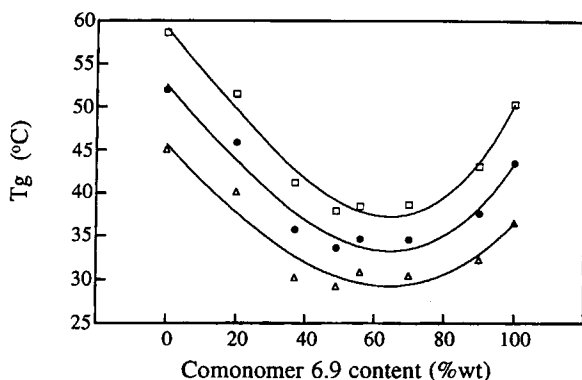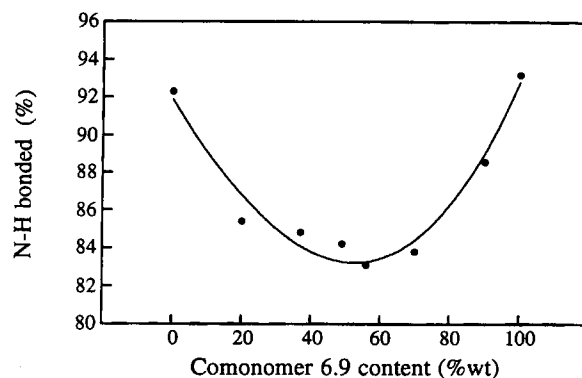
Figure 2 T_g vs. comonomer 6.9 content in copolyamides 6/6.9 after cooling from the melt at 10°C/min: (△) onset, (●) middle, (□) end.

Figure 3   Percentage of hydrogen bonded amide groups vs. comonomer 6.9 content in copolyamides 6/6.9.

amounts of monomers. These results obviously do not fit the predictions of Fox[6] or of Gordon and Taylor[21] for random copolymers that predict a monotonic change of T_g with composition, with the copolymer T_g being between the T_g values of the corresponding homopolymers. However, these results were found[22] to fit the Couchman equation[23] that takes into consideration the properties of the homopolymers and their respective alternating copolymers as well.

Hydrogen Bond Content

The percentage of hydrogen bonded amide groups vs. comonomer 6.9 content, calculated according to the Bessler–Bier method, is presented in Figure 3. The curve is U shaped and almost symmetric. The homopolyamides exhibit the highest hydrogen bond content (approximately 93%), whereas the composition of equal amounts of comonomers exhibits the lowest hydrogen bond content (approximately 83%).

It is important to mention that the amide groups' density along the copolyamide chains decreases as comonomer 6.9 content increases. Therefore, if a criterion of hydrogen bonded amide groups per weight unit is considered rather than the percentage of hydrogen bonded amide groups out of the whole amide groups in the polymer, the curve obtained will better resemble that of T_g vs. composition as in Figure 2. The copolyamides rich in caprolactam exhibit then a higher hydrogen bond content than the copolyamides rich in comonomer 6.9. The hydrogen bond content presented in Figure 3 is that in the whole semicrystalline polymer. The relative hydrogen bond content in only the amorphous phase can be evaluated using eq. (2). It is presumed that the proportion of comonomers in the amorphous phase

is similar to that in the crystalline phase and that the amide groups in the crystalline phase are fully hydrogen bonded ($[\%NH]_{crystalline} = 100$). Thus,

$$[\%NH]_{total} = \{ [\%NH]_{crystalline}*(X_c)$$
$$+ [\%NH]_{amorphous} \times (100 - X_c)\}/100 \quad (2)$$

where X_c is the percent crystallinity. According to this evaluation, the curve of relative hydrogen bond content in the amorphous phase vs. composition (not shown) is quite similar to that presented in Figure 3. Due to the low degree of crystallinity of the studied copolyamides, the values of the relative hydrogen bond content in the amorphous phase are lower by approximately 3–5% than the values obtained for the whole polymer. The FWHM of the hydrogen bonded amide groups band for the studied series is presented in Figure 4. The homopolyamides exhibit quite narrow bands and the copolymers exhibit bands of increasing width with an increase in comonomer 6.9 content. This behavior indicates a broader strength distribution of the hydrogen bonds in compositions of higher comonomer content. It is
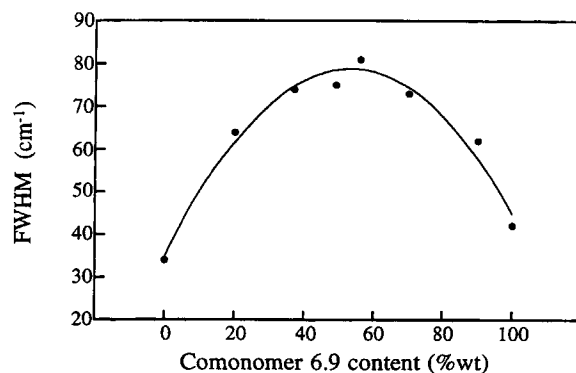
Figure 4   FWHM of hydrogen bonded amide groups band vs. comonomer 6.9 content in copolyamides 6/6.9.
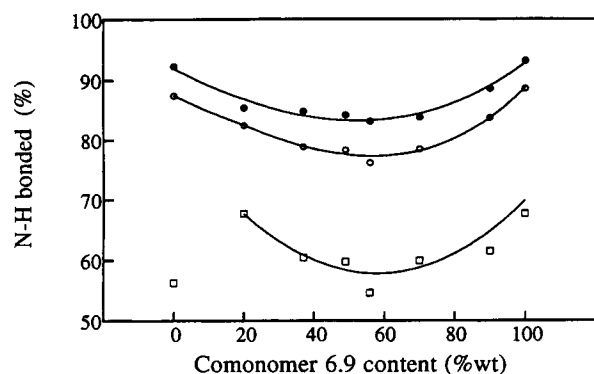
Figure 5 Percentage of hydrogen bonded amide groups in copolyamides 6/6.9 as a function of comonomer 6.9 content: (●) according to Bessler and Bier[14] method; (○) according to profile fitting, considering intensities; (□) according to profile fitting, considering areas.

assumed that to obtain 83–85% bonded amide groups in the composition of equal amounts of comonomers, distortion of segments must occur to bring most of the amide groups into bonding positions.

The profile fitting method, in addition to the Bessler–Bier method, was used to estimate the hydrogen bond content. Figure 5 shows the percentage of hydrogen bonded amide groups calculated by three different methods, as a function of comonomer 6.9 content. The profile fitting method allows the measurement of the intensity of each band separately, resulting in more accurate values than those obtained by the Bessler–Bier method. The values of hydrogen bond content obtained according to the profile fitting method are lower than those obtained by the Bessler–Bier method (by approximately 5% bonded NH). These differences are due to small deviations of the fitted from the measured curve and the drawing of a different baseline. To consider the whole range of absorptions rather than only the maximal ones, it is necessary to estimate the hydrogen bond content based on the areas under the fitted curves. The results so obtained are considerably lower, by about 15–20% bonded NH, than those obtained using the Bessler–Bier method, as shown in Figure 5. The 3300-cm^{-1} band attributed to bonded NH groups is strong and sharp; the 3450-cm^{-1} band attributed to free NH groups is weak and very broad. As a result, differences in band intensities are greater than those in band areas. Thus, the hydrogen bond contents based on the band area considerations are much lower than those obtained above and are also smaller than those commonly reported in the literature for polyamides.

As mentioned above, there are several optional values for the correction factor in eq. (1). Evaluation of the hydrogen bond content using different cor-

rection factors does not change the shape of the curve; however, lower values are obtained when the 1 : 3.2 ratio[12] is used rather than the 1 : 1.6 ratio.[14] The decrease in hydrogen bond content with comonomer content increase is more prominent when the 1 : 3.2 ratio is considered. Values for the correction factor other than those mentioned may be applied to obtain more realistic values of hydrogen bond content when the area under the absorption bands is considered.

The same general effect of copolymer composition on hydrogen bond content was obtained by the different evaluation methods, supporting the conclusion that the irregularity of amide group distribution along the random copolyamide chain results in a decrease in hydrogen bond content and in their average strength.

Effect of Hydrogen Bond Content and Degree of Crystallinity on T_g

Combination of the DSC and FTIR data clearly shows that the T_g increases with an increase in the hydrogen bond content, as depicted in Figure 6. It is clearly observed that the copolyamides can be divided into two different groups: the first one consists of the caprolactam rich copolyamides, the second consists of copolyamides rich in comonomer 6.9. The T_g dependence on hydrogen bond content is much stronger for the former group. This could stem from the higher hydrogen bond density of copolyamides rich in caprolactam; hence, a small change in hydrogen bonding causes a larger change in their T_g value.

Another factor affecting the T_g is the presence of a crystalline phase. X-ray diffraction patterns confirm that the inclusion of comonomer 6.9 into polyamide 6, or the inclusion of caprolactam into poly-
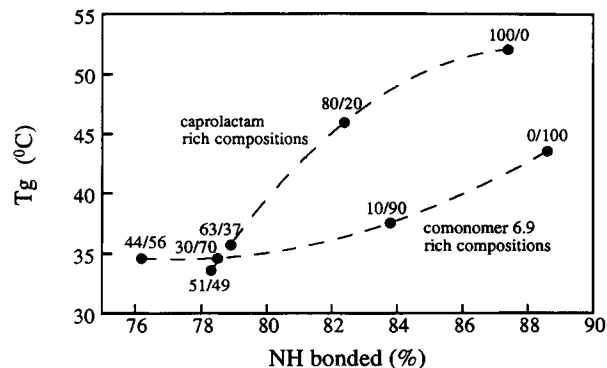
Figure 6 Glass transition temperature vs. hydrogen bond content (profile fitting, considering maximal intensities) in copolyamides 6/6.9.
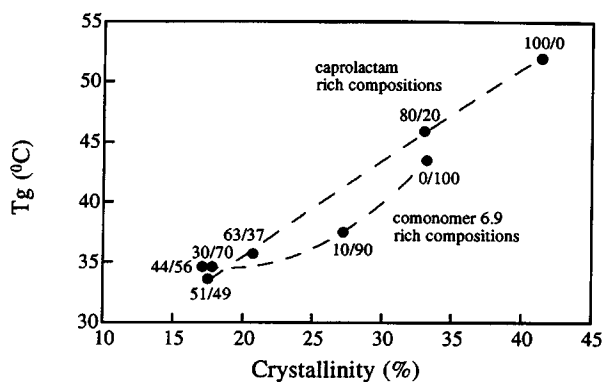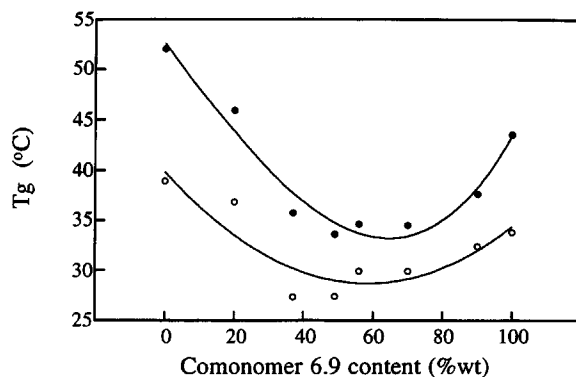
Figure 7 Glass transition temperature vs. degree of crystallinity of copolyamides 6/6.9.

Figure 8 T_g (middle point) vs. comonomer 6.9 content in copolyamides 6/6.9: (●) cooled at 10°C/min and (○) quenched.

amide 6.9, reduces the degree of crystallinity. Correlating the T_g values and the degree of crystallinity for the studied series indicate that crystals restrict the segmental mobility in the adjacent amorphous phase and thus affect the T_g at a level increasing with an increase in the degree of crystallinity, as shown in Figure 7. According to this figure, the copolymers series can be divided into the same two groups seen in Figure 6; however, the grouping here is less distinguished. A similar behavior was reported by Godovsky et al.[24] for a 6/10 copolyamide series.

Because correlations between T_g and either hydrogen bond content or degree of crystallinity were presented and neither can be altered without affecting the other, their individual effects on T_g cannot be evaluated. It is suggested, however, that hydrogen bonding has the major influence on T_g because it restricts the segmental mobility within the entire amorphous phase; whereas crystals affect only those segments located in their proximity. The latter effect may only be significant in highly crystalline polymers.

Effect of Quenching

The glass transition temperature vs. comonomer 6.9 content of the copolyamide series after slow cooling (at 10°C/min) from the melt and after quenching are depicted in Figure 8. The T_g values obtained after quenching are lower than those obtained after cooling at 10°C/min throughout the whole composition range. The more crystalline compositions (containing small amounts of comonomer) exhibit higher differences between $T_{g(10°C/min)}$ and $T_{g(quenched)}$. This phenomenon is well-known in polymers and usually stems mainly from a lower packing efficiency that is higher free volume, obtained by the rapid cooling. Similar results of $T_{g(quenched)}$ were obtained by Goodman and Kehayoglou[5] for a 6/12 copolyamide

series. In contrast, Garner and Fasulo[4] reported that the $T_{g(quenched)}$ vs. composition of a 6/12 copolyamide series gradually decreases with increasing laurolactam up to 30/70 composition, "as predicted for amorphous copolymers." In polyamides, in addition to the common effects, quenching causes a decrease in hydrogen bond content and the formation of a less regular hydrogen bond network, which decreases the T_g.

The hydrogen bond content in the presently studied series was measured after several room temperature aging times of quenched samples. The copolyamides inclined to restore their usual hydrogen bond content as the aging time increased, as shown in Figure 9 for several compositions. The homopolyamides, in comparison with the copolyamides, exhibit the highest decrease in hydrogen bond content as a result of quenching. Their retention times are the longest; but their recovery rates (the slope of the curve) are the highest, due to their greater capability for hydrogen bond formation. A similar be-
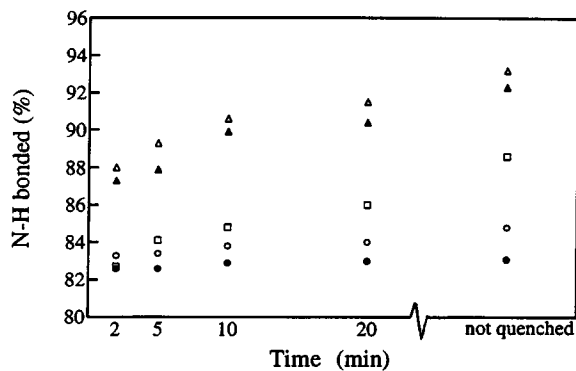
Figure 9 Percentage of hydrogen bonded amide groups vs. room temperature aging time after quenching of copolyamides 6/6.9: (▲) 100/0, (○) 63/37, (●) 44/56, (□) 10/90, (△) 0/100.

havior after quenching was reported by Hatakeyama and Kanetsuna[7] for several random 6/6.6/6.10 ter-polyamides.

SUMMARY AND CONCLUSIONS

A series of random semicrystalline copolyamides 6/6.9 was investigated. In addition to the common effects characterizing random semicrystalline copolymers, a dominant effect of hydrogen bonds on the structure and thermal behavior of their amorphous phase was demonstrated.

1. The glass transition temperature decreases as the comonomer content increases, due to a decrease in both hydrogen bond content and in the degree of crystallinity; the former has a dominant effect on T_g.
2. The hydrogen bond content decreases and their strength distribution increases as the comonomer content increases, due to the increased irregularity of the amide groups distribution along the polymer chain, as confirmed by different methods of evaluation.
3. The caprolactam rich compositions exhibit higher T_g values than those rich in comonomer 6.9. The former's T_g is more sensitive to changes in hydrogen bond content (in spite of the similarity in their measured hydrogen bond content), due to a higher amide group density.
4. Quenching in liquid N_2 of the copolyamides causes, in addition to lower efficiency of molecular packing and lower degree of crystallinity, the formation of a lower density and a less regular hydrogen bond network. These factors result in a decrease in the T_g. Following room temperature aging of quenched samples, there is a tendency of the hydrogen bonds to be restored. Higher rates of aging are obtained for the more ordered compositions, that is for the lower comonomer compositions.

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