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Amorphous Ferroelectric Polyamide Blends

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Some of crystalline polyamides having an odd number of methylene groups between successive amide bonds, for example, nylon-7 and -11,[1−4] have been reported to show ferroelectricity that generates from the crystalline region, as normal ferroelectric compounds do, but Murata, Tsunashima, and Koizumi[5−12] recently discovered the presence of ferroelectricity even in the amorphous glass state of some polyamides such as copolyamide from hexamethylenediamine and isophthalic acid (70 wt %) and terephthalic acid (30 wt %) (6I/6T) and polyamide from *m*-xylylenediamine and adipic acid (MXD6). (The chemical structures are depicted in Figure 1.) They pointed out that this unusual ferroelectricity comes from the oriented polar polyamide groups produced by an inter/intramolecular exchange of hydrogen bonding under an applied electric field and that the oriented polar amides are retained below T_g after the removal of the electric field to give a spontaneous polarization. Thus, these polyamides are unique in generating the ferroelectricity in the amorphous glass state and, hence, can afford us a new class of polymer blends of amorphous ferroelectric polyamide with other polymers or compounds, which could be useful as functional polymers. Particularly, we have much interest in studying how the ferroelectricity is changed by blending the amorphous ferroelectric polyamides with another polymer. In this work, we choose blends of two amorphous ferroelectric polyamides, 6I/6T and MXD6, as the first challenge and investigate how the blending state, such as miscibility and glass transition, and the ferroelectricity are changed by the blending ratio.

6I/6T is Selar PA3426 of Mitsui-Du Pont Polychemicals Co. (Tokyo) whose melt flow index (MI) is 3.5 under 2160 g load at 230 °C. MXD6 is MX Nylon6001 of Mitsubishi Gas Chemical Co. (Tokyo) whose MI and relative viscosity (η_r) at room temperature in H_2SO_4 are 7 and 2.1, respectively. The MXD6/6I/6T blend films were prepared by melt-extruding at 280 °C by a conventional extruder and then by quenching to room temperature onto a chill drum.

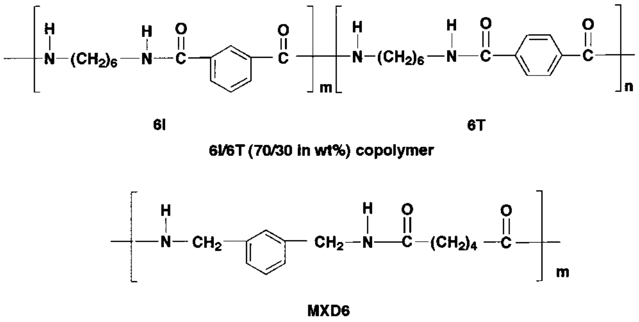

Figure 1. Chemical structures of two polyamides used here.

Thermal measurements were done at the heating/cooling rate of 10 °C min^{-1} by use of a Seiko SSC5000 differential scanning calorimeter (DSC). The transition temperatures and its enthalpy changes were calibrated using In and Sn as standards. The electric displacement (D)−electric fields (E) hysteresis was observed using the high-voltage triangular wave field of 30 mHz and 300 MV m^{-1} by means of the Sawyer−Tower method to ascertain the presence of ferroelectricity.[13] Aluminum was vacuum-deposited on both sides of films of 10−20 μm thick to make electrodes of 6.5 mm diameter. The $D-E$ hysteresis measurements were done under nitrogen atmosphere. The remanent polarization (P_r) was determined using a depolarizing current method.[6,9] The films were poled during the $D-E$ hysteresis measurements at 30 °C and then were electrically shorted at 15 °C to discharge a residual charge thoroughly, and then the depolarizing current density (j) was recorded during heating at a rate of 1.7 °C min^{-1} from 15 °C by use of a Keithley 610C electrometer and/or a Keithley 485 autoranging picoammeter.

Figure 2 shows DSC curves for MXD6/6I/6T blends at the first heating (a) and the first cooling (b). In the first heating curve for 100% MXD6, there are observed a discontinuous change near 85 °C, an exothermic peak near 149 °C, and an endothermic peak near 234 °C which correspond to T_g, a crystallization temperature (T_c), and a melting temperature (T_m), respectively. The T_c and T_m peaks are also seen for MXD6/6I/6T blends but become smaller with increasing 6I/6T content. The 100% 6I/6T copolymer does not show any T_c and T_m peaks, showing only T_g skip at 124 °C. Consequently, the quenched MXD6 is amorphous at room temperature but is crystallized near 149 °C (T_c). The formed crystallites melt at T_m (234 °C). In the blends, as MXD6 content decreases, the crystallinity is smaller, and 100% 6I/6T is amorphous. Here, one important point is that 6I/6T and MXD6 are miscible to each other over all the blending ratio, because all the blends show only one T_g in Figure 2. This good miscibility of 6I/6T and MXD6 was also confirmed by electron microscopic observations and dielectric relaxation studies.[14]

The electric displacement (D) was measured as a function of the electric field (E) at 15 °C. The $D-E$ hysteresis curves were observed for all the blends as well as 100% MXD6 and 100% 6I/6T reported previously.[5,6,9] Therefore, all the MXD6/6I/6T blends are concluded to be ferroelectric at 15 °C. In Figure 3, the

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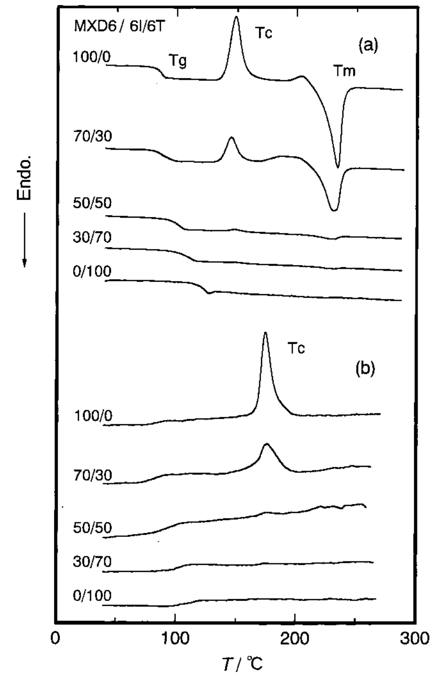

Figure 2. DSC curves for MXD/6I/6T blends at the first heating (a) and the first cooling (b).

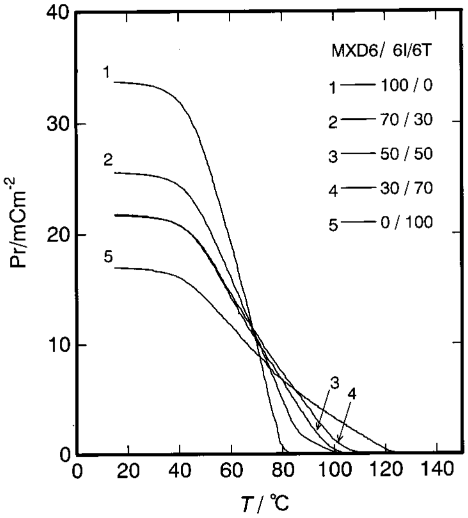

Figure 3. Temperature dependences of remanent polarization (P_r) for the poled MXD6/6I/6T blends.

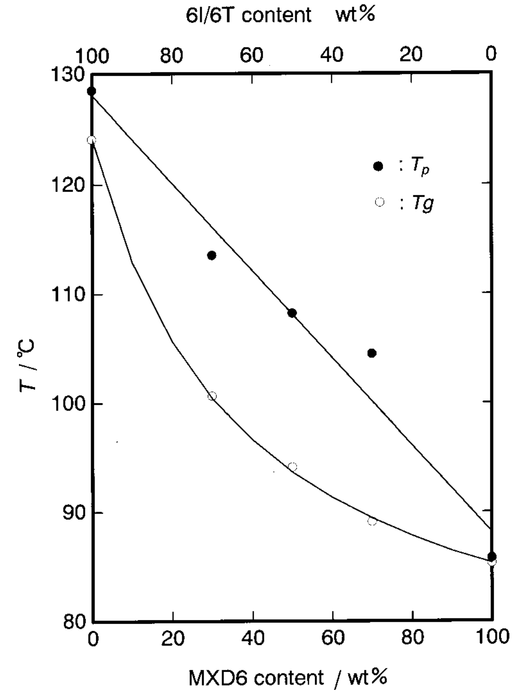

Figure 4. Plots of transition temperature (T_p) and glass transition (T_g) versus MXD6 content in MXD6/6I/6T blends: (—) for T_g is the curve estimated from the Gordon–Tayler equation with k of 3.64.

value of remanent polarization (P_r) is plotted as a function of temperature for all the blends, where the value of P_r was estimated from the depolarizing current density (j) data (heating rate: 1.7 °C min^{-1} from 15 °C). The P_r value decreases with increasing temperature, being zero at a transition temperature (T_p), reminiscent of a Curie temperature. In Figure 4, T_g and T_p are plotted as a function of MXD6 content for MXD6/6I/6T blends. The plots for T_g show a concave curve, obeying the Gordon–Tayler equation with k of 3.64,[15] $T_g = (w_1T_{g1} + kw_2T_{g2})/(w_1 + kw_2)$, where w_1 and T_{g1} and w_2 and T_{g2} are weight fraction and glass transition temperatures respectively for 6I/6T and MXD6, and k is a parameter. Here it is noted that the T_p–MXD6 content plots are on a straight line, in contrast with that of T_g, which means that T_p varies in proportion to MXD6 content.

Murata, Tsunashima, and Koizumi[6,9,11] indicated that T_p is almost consistent with T_g for amorphous polyamides; the dipole moments of the amide groups orient to the applied electric field, perhaps due to an intermolecular (sometimes intramolecular) exchange of hydrogen bonding, and the orientation is retained in the glassy state below T_g, even after the electric field is removed. The value of T_p may be closely connected with the presence of the hydrogen bonding. The dissociation of hydrogen bonding with temperature has been studied for polyamides by many reseachers[11,16,17] and in the past IR studies have been explained mostly by a thermodynamical transformation of hydrogen-bonded amides into free amides. However, the IR studies for amorphous polyamides such as poly(hexamethylene isophthalamide) (6I) by Strovanek et al.[17] pointed out that variation in IR spectra of amide groups during increasing temperature comes from a weakening in the strength of hydrogen bonding rather than a dissociation of hydrogen-bonded amides to free amides. The oriented polar amide groups are considered to be relaxed by a reorientational molecular motion of long segments above T_g, but the value of T_p would be closely connected with the strength and dissociation of hydrogen bonding. As seen in Figure 4, T_p is certainly consistent with T_g for 100% 6I/6T and 100% MXD6 but in MXD6/6I/6T blends varies in proportion to MXD6 content, being higher than T_g. From these results, it is deduced that the orientation of polar amide groups due to an exchange of hydrogen bonding by the electric field and its relaxation by removing the electric field are controlled by more local environment in the polymer matrix than the releasing of long segmental molecular motion at T_g in the blends.

In conclusion, the amorphous ferroelectric polyamide blends, MXD6/6I/6T, showed ferroelectricity in all the blending ratio, and T_p varied in proportion to the blending ratio, being higher than T_g in the blends. In this work, it was deduced that the intermolecular exchange of hydrogen bonding in the amide groups, responsible for the ferroelectricity, is controlled by more local environment than that corresponding to T_g, in the blending state. Further studies are progressing in our laboratories and will be published elsewhere in the near future.

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