Infrared spectroscopic studies of thermotropic polyamides

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SUMMARY

Poly(3,3',5,5'-tetraethyldiphenylmethane-1,18-octadecanedicarboxamide) (poly(TEDPM-ODDA)) and poly(diphenylmethane-1,18-octadecanedicarboxamide) (poly(DPM-ODDA)) are newly synthesized and found mesomorphic phase between 493 and 502 K for the former and no mesomorphic phase for the latter by use of DSC measurements and polarizing microscope observation. In the IR spectra of enantiotropic mesomorphic poly(TEDPM-ODDA), the stepwise high frequency shift of the hydrogen-bonded N-H stretching vibration in crystalline-mesomorphic and mesomorphic-isotropic liquid phase transition suggest formation of the mesomorphic state due to balancing interchain hydrogen bonding and other interchain forces. On the contrary, non-mesomorphic poly(DPM-ODDA) the N-H bands shifts to higher frequency at melting to isotropic liquid at a stretch.

INTRODUCTION

The search for thermotropic polymers for potential use as high strength fibers has concentrated on polyester.[1] Amide linkage seems an excellent candidate for the construction of durable liquid crystalline polymers since polyamides are quite chemically stable. Although polyamides are known to form lyotropic liquid crystals[2], only a few papers have reported on mesomorphic polyamides.[3] Moreover, there have been no reports on the thermotropic polyamide with only a carbon framework in the main chain except amide linkage. The most offending characteristic of aromatic polyamides is their high melting point because polyamides sometimes are decomposed before forming a mesomorphic state.[4] This is explained by the strong hydrogen bonding in the crystals.

Much attention should be given to the spectroscopic study of polyamides because interchain hydrogen bonding may play an important role in the presence of liquid crystalline phase.[5] To understand the relation between hydrogen bonding and mesogenicity the most useful technique is IR absorption spectra and the recent development of Fourier Transform IR spectroscopy has made spectroscopic study of the polymer possible. Second important motivation to study mesomorphic polyamide by IR spectroscopy is that the N-H stretching region is separated and comparatively easily analyzed theoretically[6] compared to the C=O region which is very difficult to analyze because the numerous bands are combined, which occur in studying the mesomorphic state of polyesters.[7]

From these standpoints, we try to synthesize poly(3,3',5,5'-tetraethyldiphenylmethane-1,18-octadecanedicarboxamide)(poly(TEDPM-ODDA)) and poly(diphenylmethane-1,18-octadecanedicarboxamide)(poly(DPM-ODDA)) and
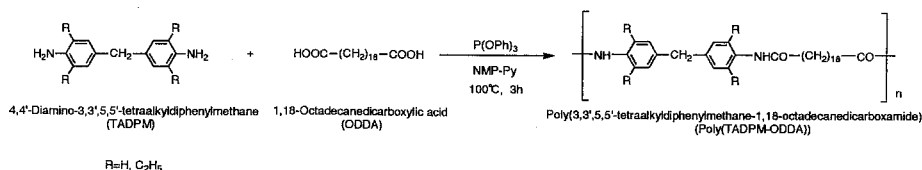
Figure 1. Synthetic route of polyamides.

studied their phase transition and mesogenicity by DSC measurement and polarizing microscope observation, and especially studied the relation between mesogenicity and hydrogen bonding by the use of FT-IR spectroscopy.

EXPERIMENTAL

Synthesis[8]
     Synthesis of the polyamides were done by the direct polymerization of 4,4'-diamino-3,3',5,5'-tetraethyldiphenylmethane(TEDPM) or 4,4'-diamino-diphenylmethane(DPM) and 1,18-octadecanedicarboxylic acid(ODDA) in the presence of triphenylphosphite. TEDPM and DPM(supplied from Nippon Kayaku Co., Ltd.) was recrystallized from methyl ethyl ketone and ODDA(supplied from The Nisshin Oil Mills Co., Ltd.) was from methanol before use. The synthetic route of polyamides was shown in Fig. 1. The obtained polymers were washed by methanol. The polymers were identified as objectives by FT-IR. The limiting viscosity of the polymer was measured by use of an Ubbelohde's viscometer at 303 K.

Measurements of Physical Properties
     Thermal properties of the polyamides were measured by use of a Perkin Elmer DSC 1B with a heating/cooling rate of 10 K min^{-1} from room temperature to over the melting point. The texture of the mesomorphic state was observed by use of a polalizing microscope, Nikon Optiphoto-pol XTP-11 equipped with a Mettler FP-82 hot stage with a heating/cooling rate of 10 $Kmin^{-1}$ under crossed polarizers. Temperature dependence of IR spectra was measured by a Perkin Elmer FT-IR 1600 using a temperature-controlled optical cell(OMRON H-32 Heater) with a Omron E5T temperature controller. Spectra were measured for KBr disks of polyamides between 450 and 4000 cm^{-1} in a temperature range from room temperature to over the clearing point in the heating process.

RESULTS AND DISCUSSION

DSC measurements and Polarizing Microscope Observation
     In Fig. 2 DSC thermograms of poly(TEDPM-ODDA) and poly(DPM-ODDA) are shown. In poly(TEDPM-ODDA) we observed two endothermic peaks around 493 and 502 K in the first heating process and only one exothermic peak was shown at 469 K in the first cooling process. On the polarizing microscope observation a mesomorphic schlieren texture was observed between the two endothermic peaks in the first heating and below the temperature of exothermic peak in the first cooling.[9] In the second heating process a small exothermic peak subsequent endothermic peak is found around 439 K and this is the characteristic of glass transition. In the first cooling below this glass transition region, the schlieren texture was still observed especially at room temperature and poly(TEDPM-ODDA) became glassy mesomorphic state. On the contrary, poly(DPM-ODDA), which has no prominent

groups in the ortho position of the phenyl ring with adjacent to hydrogen bonding of amide linkage, has no mesomorphic state in polarizing microscope observation. In the first heating of DSC thermogram of poly(DPM-ODDA), three endothermic peaks were observed at 487, 496 and 507 K. The lower-temperature two peaks correspond to crystallin-crystalline phase transitions in the polymer and higher temperature one to melting into isotropic liquid. In the first cooling only one exothermic peak, which corresponds to freezing, was observed at 476 K.

IR spectra and mesomorphism

The N-H stretching region of polyamides spans a range of about 3100-3500 cm^{-1}. The temperature dependence of IR spectra of poly(TEDPM-ODDA) is shown in Fig. 3. At room temperature the poly(TEDPM-ODDA) exhibits two infrared bands at 3450 (very weak shoulder) and 3266 cm^{-1} (relatively sharp). In poly(DPM-ODDA) also shows two infrared bands at 3450 (very weak shoulder) and 3310 cm^{-1}. The very weak shoulders and relatively sharp bands are assigned to "free" and "hydrogen-bonded" N-H stretching mode, respectively.[10] Our report concentrates on the hydrogen-bonded N-H stretching vibration because the absorption intensity of the IR spectrum of free N-H bonding is much smaller than that of the hydrogen-bonded one. Temperature dependence of the peak of hydrogen-bonded N-H stretching vibration of poly(TEDPM-ODDA)(white circle) and poly(DPM-ODDA)(black circle) are shown in Fig. 4. With increasing temperature, the peak maximum of the hydrogen-bonded N-H stretching bond of poly(TEDPM-ODDA) shifts to a higher frequency approximately linearly. The hydrogen-bonded N-H stretching vibration shifts to an even higher wave number with an increase in the temperature in the neighborhood of melting point in premelting effect. At 493 K with
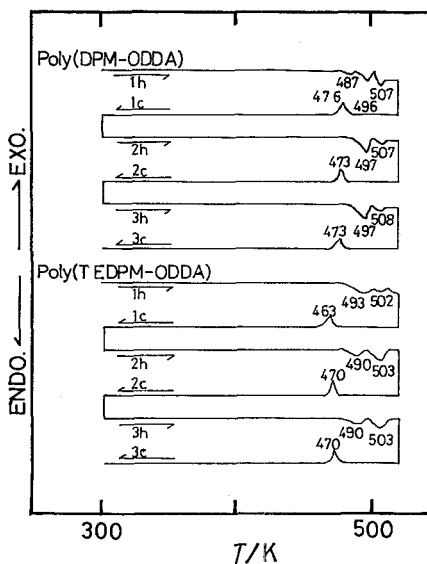

Figure 2. DSC thermograms of poly(TEDPM-ODDA) and poly(DPM-ODDA).
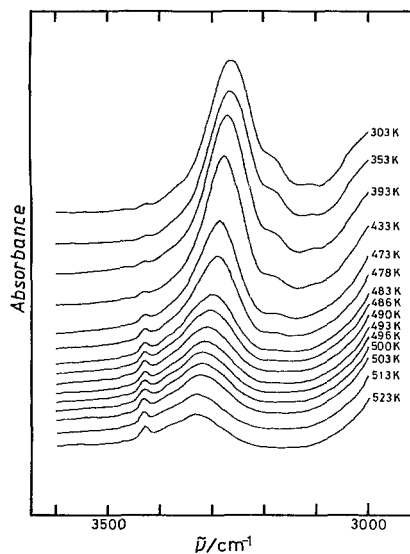
Figure 3. Temperature Dependence of IR spectra of poly(TEDPM-ODDA).

poly(TEDPM-ODDA). This is due to a slightly increasing temperatures

hydrogen-bonded N-H stretching vibration abruptly shifts to a higher wave number by 25 cm^{-1} which corresponds to the phase transition from crystalline state to mesomorphic one(T_m) found by DSC and polarizing microscope observation. The strong shifts to higher frequencies in going from the crystalline state to mesomorphic state has to be related to a decrease in hydrogen bonding. The N-H stretching vibration shifts 15 cm^{-1} to a high wave number at 502 K which corresponds to phase transition from mesomorphic to isotropic liquid state(T_{M-I}). In the isotropic liquid state the value of hydrogen-bonded N-H stretching vibration is 3390 cm^{-1} and is also smaller than the free N-H stretching vibration. These results show that the hydrogen bonding in the isotropic state in poly(TEDPM-ODDA) weakens much more than the crystalline state but is still present in the isotropic liquid state.

Figure 4. Temperature dependence of N-H stretching vibration of poly(TEDPM-ODDA): and poly(DPM-ODDA): .

In the temperature dependence of N-H stretching vibration in poly(diphenylmethane-1,18-octadecanedicarboxamide) (poly(DPM-ODDA)), which has no mesomorphic transition, only one high frequency shift(15 cm^{-1}) occurs at 489 K, which corresponds to melting from crystalline to isotropic liquid state. On the other hand, in the poly(TEDPM-ODDA) the hydrogen bonding weakens by steps from crystalline to mesomorphic state and from mesomorphic to isotropic liquid state. In poly(TEDPM-ODDA), the temperature dependence of N-H stretching vibration is very large and this result show that the hydrogen bond weakens with the increase of temperature due to increasing thermal vibration of ethyl group of the benzene ring adjacent to amide linkages. In the medium of the process of weakening in hydrogen bonding, the intermediate mesomorphic state is present just to balance the intermolecular forces. On the contrary in poly(DPM-ODDA), the temperature dependence of hydrogen bonding is very slight and the relatively rigid hydrogen bonding just below the melting point weakens at a stretch in the melting from crystalline to isotropic liquid phase transition. In this case the phase behavior with the molecular weight dependence does not need to be taken into consideration because the values of intrinsic viscosity of poly(DPM-ODDA) and poly(TEDPM-ODDA) in sulphuric acid are 0.14 and 0.18 cm^{3}g^{-1} and almost equivalent.

In conclusion, the hydrogen bonding in poly(TEDPM-ODDA) with adjacent ethyl groups to amide linkages is relatively strong at room temperature but weakens with increasing temperature due to the vibrational motion of the ethyl groups and weakens by steps from crystalline-mesomorphic and
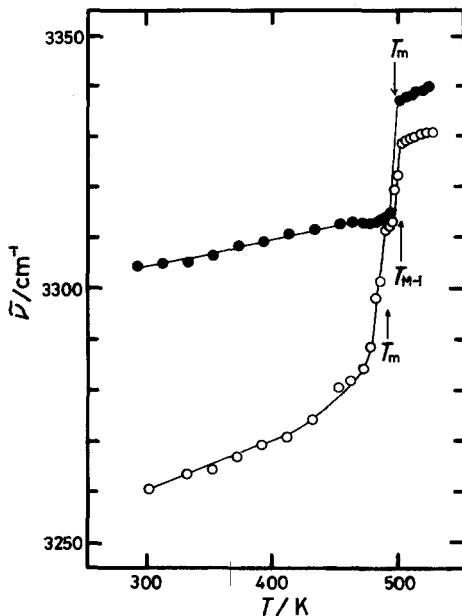
mesomorphic-isotropic liquid phase transitions. On the contrary, poly(DPM-ODDA) without mesomorphic state has a weaker hydrogen bonding at room temperature and has a slight temperature dependence till reaching melting temperature to isotropic liquid where the N-H hydogen bonding weakens at a stretch. Poly(TEDPM-ODDA) may have a mesomorphic state at balancing the N-H hydrogen bonding and other interchain forces.

ACKNOWLEDGEMENT

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