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Spectroscopic study of lyotropic liquid crystal polymer in H_2SO_4

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Summary

The molecular structure of lyotropic liquid crystal polymer polybenzamide in H_2SO_4 has been studied by FTIR. The polyethylene film was used as window material to overcome the obstacle of solvent corrosion. The result indicate that the polybenzamide is protonated at the carbonyl position in H_2SO_4. This is also helpful to explain the dissolution mechanism of polybenzamide and other lyotropic liquid crystal polymer in acid solution.

Introduction

The study of lyotropic liquid crystal polymers have been continued in last decade.[1] A great deal of structural data in bulk state have been accumulated by many physical chemistry methods. One aspect which has been generally overlooked is the structure of these polymers in solution. It is known that the high strength of these polymers are mainly obtained from the high orientation degree of molecular chains during fibre processing from anisotropic liquid crystalline phase. The information on the polymer structure in solution is expected both from technological and academic point of view. The lack of such a study might be due to the only known solvent for these polymers are powerful acid such as sulfuric acid which are strong corrosive. It prevented attempts to obtain structural information in solution by spectroscopic methods. In this short communication, we present infrared spectroscopic study on the lyotropic liquid crystal polybenzamide in H_2SO_4 solution.

Experimental

In order to take the infrared spectra of the polymer in acid solution, one has to, first of all, overcome the obstacle of the solvent corrosion to sample cell. We had tested many window materials and attempted to find one possessing two character both anti-corrosive and transparent in the interesting spectrum region. It was finally found that

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*To whom offprint requests should be sent the polyethylene film is suitable to this purpose. Although sulfuric acid can oxidize the polyolefin, however, at the limited time needed for preparation of solution specimen and spectrum measurement (less than 2 minutes), the oxidization of polyethylene film can be neglected and had no effect on the spectrum measurement. Thus, we used polyethylene film as the window material for support the polymer solution.

The spectrum of polybenzamide in sulfuric solution from 2000cm^{-1} to 1500cm^{-1} region is shown in Figure 1. The spectrum at other regions is not displayed for the strong absorption bands associated with solvent masked the bands of polymer. We did try to obtain the spectra of the polymer in other regions using the method of digital absorbance subtraction, but the results are not satisfied as the bands are strongly modified by the solvent and could not be distinguished definitely from solvent bands.

The spectra were recorded by the BRUKER IFS-113V FTIR spectrometer which is a vacuum type interferometer with liquid nitrogen cooled MCT detector. The environmental interference is essentially eliminated. Each spectrum was 64 scans averaged. The spectral resolution was set at 2cm^{-1} and the scan velocity was taken at the highest of the instrument for shorting the time of collecting the interferograms.

The polymer sample was dissolved by 98% H_2SO_4 to form a solution of 9% concentration in weight which is in liquid crystal phase region. The prepared solution specimen was then injected into the polyethylene film cell and the cell was sealed immediately to avoid the moisture. The specimen was unoriented. The spectrum was then measured instantly. The background spectrum of the sulfuric acid and the cell was recorded in the same way.

Results and discussion

As can be seen from figure 1, the curve B is the spectrum of the polybenzamide in sulfuric acid solution. For the comparison with the structure in the bulk state, the spectrum of the unoriented sample in solid film is displayed as curve A. The curve C is the background spectrum of the cell and sulfuric acid. It is evident that they are transparent in the region from 2000cm^{-1} to 1500cm^{-1}. The significant difference of the two spectra in different state is apparent. The carbonyl stretching mode shifts to lower frequency 1646cm^{-1}, 14cm^{-1} shift from bulk film to solution. But the benzene ring C=C stretching near 1600cm^{-1} shifts to higher frequency region and changes its band shape. At the amide-II band area, a band at 1520cm^{-1} is disclosed in the solution state, while at the bulk film, the amide-II band is overlapped with the strong band at 1506cm^{-1} which is due to the C=C stretching mode. These spectral differences between bulk film and solution imply strongly that the polybenzamide chain structure is significantly modified by solvent.

It has been postulated that liquid crystal polymer in strong acid exist in protonated form[2] , but the location of the charge and the change in structure are unknown. From the above spectra, one can suggest that the location of the proton is at the position of carbonyl group and the proton of the solvent bonded with the oxygen in carbonyl which has a pair of sole electrons. The carbonyl band shifts to lower frequency may be caused directly by forming stronger bond

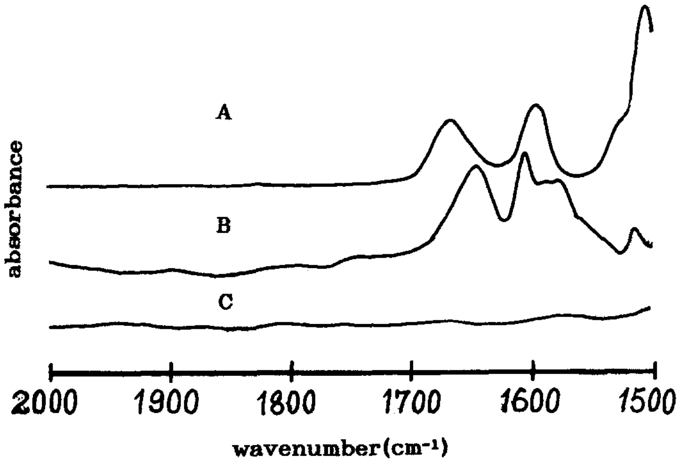

Figure 1. The infrared spectra of polybenzamide at different state at the spectrum region from 2000cm^{-1} to 1500cm^{-1}. A, PBA spectra in solid film. B, PBA spectrum in H_2SO_4 solution. C, the background spectra of the cell window material and the solvent H_2SO_4.

Table 1. The band behavior of polybenzamide in different states and different temperature.

Frequency Film 25°C	Frequency Film 250°C	Frequency In H_2SO_4	Vibrational Mode
1658cm^{-1}	1661cm^{-1}	1646cm^{-1}	C=O stretching
1603cm^{-1}	1601cm^{-1}	1607cm^{-1}	C=C stretching
1592cm^{-1}	1589cm^{-1}		C=C stretching

between oxygen and proton than the hydrogen bond among the amide groups on polymer chains. This might be analogue to the case of the polybenzamide in DMAc/LiCl solution where the lithium ions coordinated with carbonyl group of polymer chain and led the carbonyl mode shift to lower frequency[3]. The result is also agree well with the Raman study on Poly(p-phenylene benzbisthiaszole) in H_2SO_4 where the PBT chain is protonated at the C=N double bond position[4].

For better understanding the structural changes, we measured the temperature dependence of spectra of polybenzamide film. The interested bands behavior with temperature are listed on Table 1. It can be seen that the carbonyl band shift to higher frequency, while the benzene ring C=C stretching mode moves to lower frequency with elevating temperature. This temperature effect is just opposite to the case of solution. It is believed that the polybenzamide chains associated in the bulk state by forming hydrogen bonds. The carbonyl mode shown a higher frequency shift means that the hydrogen bond between chains are weakened at higher temperature. This is in accordance with the results of the normal vibration calculation of polybenzamide[5] that the frequency changes of the stretching mode are mainly caused by changes in intermolecular interactions. There is no significant variation in intramoleculer structure during temperature change for polybenzamide chain.

It is well known that the cross-conjugation is the main mechanism stabilizing the chain backbone. The twin band near 1600cm^{-1} are considered to be sensitive to the cross-conjugation[6]. The two bands have a same intensity in the conjugated form and the band at lower frequency side will reduce its relative intensity when there is little conjugation effect with adjacent group. Therefore, the C=C stretching mode modified its shape at solution is a direct evidence that the cross-conjugation reduced from bulk to solution.

The spectra results is also helpful to elucidate the dissolution mechanism of polybenzamide in acids. The dissolution of solid sample requires to break the strong hydrogen bonding among amide groups on the chains. A stronger bonding between proton and the sole electrons of carbonyl oxygen replaced the hydrogen bond and facilitate the dispersion of polymer chains. The proton play an important role as the lithium ions in the case of DMAc/LiCl solvent where the lithium ions coordinate with the carbonyl group instead of the hydrogen bonds between chains and led the polybenzamide chains to be dissolved in solution.

From the above discussion, it is concluded that the spectra of liquid crystal polymer polybenzamide in sulfuric acid could be obtained with polyethylene as a window material. This method can also be extended to other lyotropic liquid crystal polymer solution using strong acid as solvent. The polybenzamide chain has been protonated at the carbonyl position. The spectra data can be used to explain the dissolution mechanism of lyotropic liquid crystal polymer in acid solution.

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