

Solvent Induced Crystallization of Syndiotactic Poly(Methyl Methacrylate) Relation to the Formation of Polymer Aggregates in Solution

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Summary

Solutions of syndiotactic (s) poly(methyl methacrylate) (PMMA) and samples of solid s-PMMA prepared from these solutions were studied by NMR and infrared (IR) spectroscopy and by wide-angle X-ray scattering (WAXS). IR spectra of s-PMMA films obtained from o-dichlorobenzene solutions by evaporation of solvent at room temperature have shown that the ordering of polymer chains which exists in aggregates of s-PMMA in o-dichlorobenzene is preserved in the solid state. s-PMMA prepared in this way is characterized as partly crystalline by WAXS. When o-dichlorobenzene is evaporated at elevated temperatures at which the aggregates of s-PMMA are decomposed, or if solid s-PMMA is obtained from solutions in which aggregation does not take place, the obtained solid polymer is amorphous.

Introduction

Our previous NMR studies of stereoregular PMMA in solution have shown that in some solutions s-PMMA forms associated structures (SPĚVÁČEK and SCHNEIDER 1974, 1975, 1980, SPĚVÁČEK 1978, SPĚVÁČEK et al. 1982, MRKVIČKOVÁ et al.). Aggregation of s-PMMA in solution was also proved by osmometry, viscometry and light scattering (SPĚVÁČEK et al. 1982, REHAGE and WAGNER, MRKVIČKOVÁ et al.). In the cited papers it was shown that aggregation depends strongly on the degree of stereoregularity and on the solvent. Aggregation takes place as a result of the interactions of long parallel s-sequences; in some solvents (e.g. o-dichlorobenzene), the content of the aggregates of s-PMMA is quite high, even in dilute solutions, whereas in other solvents (e.g. acetonitrile), the tendency to aggregation of s-PMMA is negligible.

In order to find out if the aggregation appearing in some solutions of s-PMMA also affects the structure of s-PMMA in the solid state, we have studied solutions of s-PMMA in o-dichlorobenzene at various temperatures by means of NMR and IR spectra, and s-PMMA films prepared in various ways by means of IR spectra and WAXS diagrams.

Experimental

Polymer. s-PMMA was prepared by coordination polymerization in toluene at -78°C , initiated by triethylaluminum and TiCl_4 and terminated by HCl /methanol. The reaction mixture was diluted by chloroform, the polymer was precipitated into methanol and repeatedly washed by HCl /methanol and finally only by methanol. The polymer was redissolved in chloroform, reprecipitated in methanol and dried at 40°C and 66 Pa. The polymer prepared in this way will in the following be designated as virgin s-PMMA. Analysis of ^1H NMR spectra has shown that this s-PMMA contains 89.5% syndiotactic, 8.5% heterotactic and 2% isotactic triads. The osmometrically determined number-average molecular weight $M_n = 145\,000$. According to gel-permeation chromatography in tetrahydrofuran this s-PMMA exhibits a single-peak distribution of molecular weights, with $M_w/M_n = 1.6$.

NMR spectra. High-resolution ^1H NMR spectra were measured on the spectrometer PS-100 JEOL at 100 MHz. The integrated band intensities were determined with the accuracy of $\pm 1\%$. Solutions of s-PMMA in o-dichlorobenzene and CD_3CN (concentration 10% (w/v)) were homogenized at 100°C for one day, and left standing at room temperature for several days before measurement.

IR spectra. IR spectra were measured on the spectrometer Perkin-Elmer 621 and treated by the multichannel data analyzer TN-4000 Tracor Northern. The solutions of s-PMMA in o-dichlorobenzene and acetonitrile were prepared in the same way as for the measurement of NMR spectra. s-PMMA films of several μm thickness were prepared by evaporation of solvent from these solutions (at room temperature under vacuum) on AgCl or KBr pellets. Films prepared in this way did not contain any solvent as proved by IR spectra in which no solvent band could be detected. IR spectra of virgin s-PMMA in nujol mull were also measured for comparison.

WAXS. X-ray scattering was measured with the Hilger and Watts diffractometer and with a flat-film camera, using $\text{CuK}\alpha$ radiation. Samples of solid s-PMMA for WAXS were obtained by evaporation of solvent from solutions of s-PMMA in o-dichlorobenzene (concentration 1% w/v) and in acetonitrile (concentration 10% w/v) prepared in the same way as for the measurement of NMR spectra. As compared to IR, a much larger amount of sample was necessary for WAXS (~ 50 mg), and therefore the samples contained 15% w/w of o-dichlorobenzene (11 mole % as related to a monomer unit) even after 3 weeks of vacuum evaporation at room temperature; in this case solvent bands could be detected in IR spectra. The samples of s-PMMA from acetonitrile did not practically contain any solvent. Virgin s-PMMA was also measured for comparison.

Results and Discussion

As the ^1H NMR bands of aggregated units of s-PMMA are so broad that they cannot be detected in high-resolution ^1H NMR spectra, it is possible to determine the fraction p of aggre-

gated monomer units from a comparison of the absolute values of integrated band intensities in high-resolution ^1H NMR spectra (SPĚVÁČEK and SCHNEIDER 1975, 1980, SPĚVÁČEK 1978, SPĚVÁČEK et al. 1982, MRKVIČKOVÁ et al.). The temperature dependence of the fraction p for s-PMMA in o-dichlorobenzene is shown in Fig.1. From this figure it is evident that at room temperature the greater part (73%) of s-PMMA is present in the aggregated state, but the fraction of the polymer in the form of molecular solution is also not negligible (27%). Decomposition of aggregates takes place in the range 35-60°C, above 60°C no associated structures of s-PMMA are present in o-dichlorobenzene. Measurements of ^1H NMR spectra do not indicate any aggregates in the solution of s-PMMA in CD_3CN ($p \lesssim 0.05$).

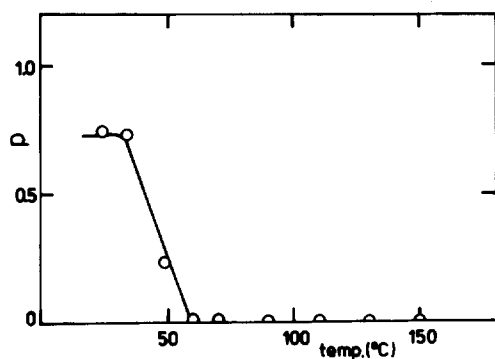
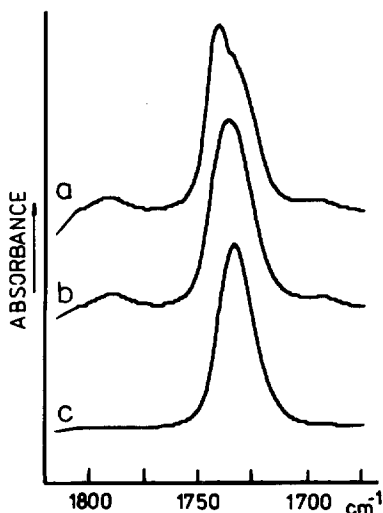


Fig.1. Temperature dependence of the fraction p of aggregated monomer units of s-PMMA in o-dichlorobenzene

As seen from Fig.2, aggregation of s-PMMA is also manifested in IR spectra. In IR spectra of s-PMMA dissolved in o-dichlorobenzene and measured at 60°C, where according to NMR

Fig.2. IR spectra (range of C=O stretching vibrations) of s-PMMA solutions in o-dichlorobenzene at 25°C (a), in o-dichlorobenzene at 60°C (b), in acetonitrile at 25°C (c).



spectra all aggregates are decomposed, the band of the C=O stretching vibration has a symmetrical shape (Fig.2b) similarly as in IR spectra of solutions of s-PMMA in acetonitrile (Fig. 2c) and in chloroform, where association also does not take place (SPEVÁČEK and SCHNEIDER 1975). In IR spectra of the solution of s-PMMA in o-dichlorobenzene measured at room temperature, a new band at higher wavenumber appears in the range of C=O stretching vibrations, in addition to the band mentioned above (Fig.2a). As the intensity of this band changes with temperature similarly as the value p indicating the degree of aggregation as determined from NMR spectra, it is evident that this new band at higher wavenumber corresponds to C=O stretching vibrations in aggregated monomer units. We assume that this new band is generated in consequence of the regular ordering of ester groups in the aggregated state.

The same range of IR spectra measured in films of s-PMMA prepared by evaporation of solvents from solutions is shown in Fig.3. For films prepared from solutions where aggregation of s-PMMA does not take place (acetonitrile), or at temperatures where the aggregates are decomposed (from o-dichlorobenzene at 110°C), IR spectra exhibit a single symmetrical band in the range of C=O stretching vibrations, at 1731 cm^{-1} (Fig.3b,d). The situation is the same for virgin s-PMMA measured in nujol mull. IR spectra of the s-PMMA film prepared from o-dichlorobenzene solution by evaporation of solvent at room temperature, exhibit a further band at 1741 cm^{-1} , in addition to the band at 1731 cm^{-1} (Fig.3a); the wavenumber of this band is equal to that of the band of aggregated s-PMMA units in o-dichlorobenzene solution (Fig.2a). The results obtained from IR spectra thus indicate that the mutual ordering of polymer segments formed by aggregation of s-PMMA in o-dichlorobenzene solutions, is preserved in the solid state, provided that

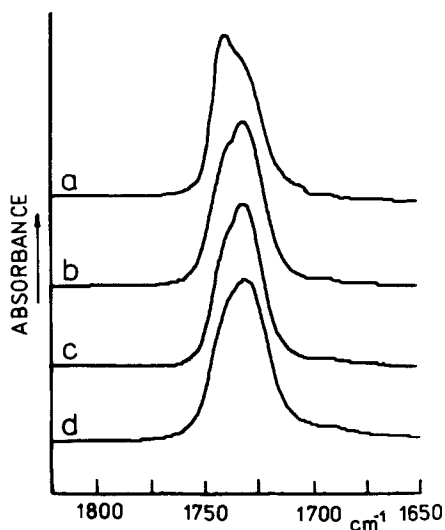


Fig.3. IR spectra (range of C=O stretching vibrations) of s-PMMA films measured at 25°C: Film prepared from o-dichlorobenzene by evaporation at 25°C (a), from o-dichlorobenzene at 110°C (b), from acetonitrile at 25°C (d). Film (a) heated to 150°C before measurement (c)

evaporation has taken place at temperatures at which the aggregates of s-PMMA are stable (see Fig.1). The ordering of s-PMMA in the solid state disappears at higher temperatures, in dependence on the content of residual solvent in the film. For a film containing no residual o-dichlorobenzene, order was completely lost after heating of the film to 150°C (Fig.3c). For a film containing about 25% w/w of o-dichlorobenzene, IR spectra indicated total loss of order already after heating to 94°C.

We have attempted to determine the content of ordered s-PMMA both in the solution of s-PMMA in o-dichlorobenzene at 25°C and in the film prepared from this solution, from comparison of the integrated intensities of the bands in the range of C=O stretching vibrations. The two bands were separated under the assumption of Lorentzian band shape and equal integral absorbance coefficients. This procedure yielded the fraction of ordered s-PMMA in o-dichlorobenzene solution as equal to 47%, in the solid state to 45%.

The WAXS diagrams of the samples of solid s-PMMA are shown in Figs 4 and 5. Contrary to the films of s-PMMA studied by IR spectroscopy, the sample of s-PMMA prepared by evaporation of o-dichlorobenzene at room temperature contained 11 mole % of solvent. The shape of the C=O stretching band in IR spectra was not affected by this and was the same as in Fig. 3a. From Fig.4 it is evident that while the virgin s-PMMA appears as completely amorphous in the X-ray diagram (similarly as the s-PMMA prepared from acetonitrile solution), the s-PMMA prepared from o-dichlorobenzene solution by room-temperature evaporation exhibits a crystalline X-ray pattern. Such crystalline X-ray pattern is not observed when the solvent was evaporated at 105°C. From the broadening of the crystalline

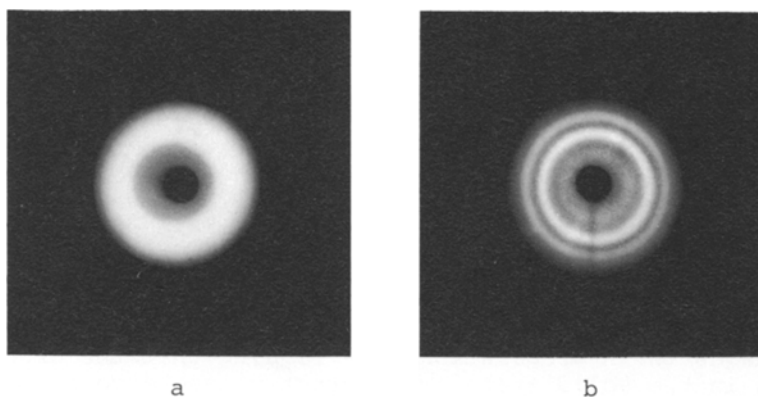


Fig.4. WAXS pattern of virgin s-PMMA (a), s-PMMA prepared from o-dichlorobenzene solution by evaporation of solvent at room temperature (b)

reflections (Fig.5), corrected for instrumental broadening, the size of the crystallites was estimated as 5.7 nm. After separation of the amorphous component of the scattering, using the shape from virgin s-PMMA (Fig.5), the degree of crystallinity of s-PMMA prepared by room-temperature evaporation from o-dichlorobenzene solution was determined as 29 weight %.

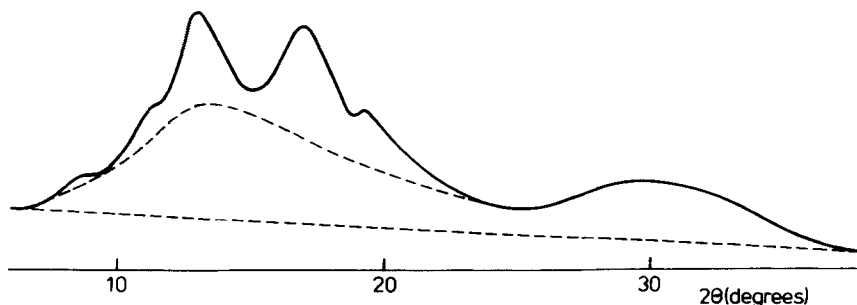


Fig.5. WAXS diagram of s-PMMA prepared from o-dichlorobenzene solution by evaporation of solvent at room temperature. Dashed line indicates the amorphous component, obtained with the shape of virgin s-PMMA or s-PMMA from acetonitrile solution

As the solvent also contributes to the amorphous component, the actual value of crystallinity may be somewhat higher. Considering that each of the applied methods indicates a different manifestation of the ordering of s-PMMA (the fraction of s-PMMA monomer units with hindered mobility in NMR, mutual ordering of ester groups in IR and regular ordering of polymer chains in WAXS), the agreement of the quantitative data characterizing order in solutions and in the solid state can be considered as good.

The results of this study indicate a relation between the state of the s-PMMA molecules in solution and the structure of s-PMMA in the solid state. Removal of solvent from solutions of s-PMMA where most monomeric units are aggregated generates crystalline structure; from solutions where aggregates of s-PMMA do not exist, amorphous polymer is obtained. The finding that the aggregated stage of s-PMMA in solution is a prerequisite for the formation of crystalline s-PMMA was also proved for other solvents (e.g. toluene); a detailed study considering also the conformational structure of ordered s-PMMA chains is in preparation. The finding that the ordering of s-PMMA in the solid state is a direct consequence of molecular interactions of s-PMMA in solution points to the importance of solution studies for the understanding of the generation of crystalline forms in polymer systems.

In a recent publication, KUSUYAMA et al. describe the preparation of oriented crystalline samples of s-PMMA by absorption of chloroacetone or diethylketone vapours at room

temperature. From the observation that evaporation of the solvent at 120°C leads to loss of crystallinity (a decrease of crystallinity was observed even for prolonged standing at room temperature) these authors conclude that the solvent directly stabilizes the crystalline structure of s-PMMA e.g. by the formation of a complex with s-PMMA, similar to the well known amylose-iodine complex. From our results (especially from IR spectra, where the studied films of s-PMMA contained practically no solvent) the existence of the crystalline form of s-PMMA is not conditioned by the presence of the solvent. Also we did not observe any change in the shape of the X-ray diffractogram of a partly crystalline s-PMMA sample after being kept for 3 months at room temperature. In our opinion, a suitable solvent only promotes a stable mutual interaction of long s-sequences (aggregation stage), simultaneously affecting the conformational structure of s-PMMA chains, and thus makes possible subsequent crystallization. Crystalline s-PMMA is not formed when the solvent is evaporated at elevated temperatures where aggregation does not take place.

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