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AN ELECTRON MICROSCOPY STUDY OF STEREOCOMPLEX FORMATION BY POLY(METHYL METHACRYLATE)

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ABSTRACT
A study was made of stereocomplex formation by a mixture of isotactic and syndiotactic samples of poly(methyl methacrylate) in tetrahydrofuran. Specimens were isolated from solution at various times and examined by electron microscopy after first evaporating off the solvent. Initially, globular particles were found; later, branched fibrillar stuctures were observed. Finally, the stereocomplex particles started to form microgel. The structural development which was observed to occur explains the apparently diverse results of some earlier studies.

INTRODUCTION

The formation of stereocomplexes between isotactic and syndiotactic poly(methyl methacrylate) has been the subject of numerous studies, particular attention having been directed towards solution behaviour (1-11). Investigations have been made of the effect of solvent type (4,12, 13), total polymer concentration (14,15), weight ratio of the polymers (6,16,17), tacticity (6,18), temperature (5,14,19,20) and time (11,15,19,20). The texture of the stereocomplexes formed in solution is affected by the strength of the polymer/solvent interactions since the latter govern the minimum stereoregular length required for stereocomplex formation and therefore the degree of compactness of the stuctures (6,13).

Challa et al. (19,21) studied stereocomplex formation between isotactic and syndiotactic poly(methyl methacrylate) in solution using viscometry, osmometry, light scattering and gel permeation chromatography. It was suggested that three stages of complex formation could be distinguished. First, when dilute solutions of the isotactic and syndiotactic polymers are mixed, stereosequences of the chains complex locally, the ratio of isotactic/syndiotactic sequences being 1:2 for the polymer tacticities studied by Challa et al. Second, the stereocomplexed sequences aggregate further leading to compact particles of the order of 10-100nm in length; third, the compact particles aggregate further to form larger structures. Mekenitskaya et al. (22) suggested on the basis of flow birefringence measurements that the primary stereocomplex particles are rod-like and that aggregates formed by the latter consist of three or four uniformly oriented particles. On the other hand Katime and Quintana (18), interpreting light scattering measurements made at the outflow of a gel permeation chromatography system, showed that the stereocomplex particles could be adequately described by a model having a segment distribution lying between that of a gaussian coil and a sphere.

We now report an electron microscopy study of stereocomplex formation by a mixture of isotactic and syndiotactic samples of poly(methyl methacrylate) in tetrahydrofuran. The process occurs relatively slowly in tetrahydrofuran compared with some of the other solvents which are complex supporting, making it possible to monitor the changes occurring in solution. For the same reason, syndiotactic polymer with a content of syndiotactic triads of only 75% was used; preliminary studies with a sample having a content of syndiotactic triads of 95% were

unsatisfactory because the formation of microgel occurred too quickly.

EXPERIMENTAL

Materials. Isotactic PMMA was prepared by anionic polymerization in toluene at -78°C with phenyl magnesium as initiator (23). Syndiotactic PMMA was prepared by anionic polymerization in tetrahydrofuran initiated with butyl lithium (24).
The polymers were fractionated using benzene/methanol as a solvent/non-solvent mixture. Weight-average molecular weights, $\overline{M}_w$, measured by laser light scattering were determined in ethyl acetate at 25°C. Gel permeation chromatography measurements were carried out in tetrahydrofuran at 20°C with two u-Shodex columns (A80M) calibrated with polystyrene standards. The tacticities of the PMMA fractions were determined by ^{1}H-NMR on chloroform solutions at 45°C using a 200 MHz Bruker Spectrometer.
The value of $\overline{M}_w$ of the isotactic fraction chosen for study was 2.2×10^5 and $\overline{M}_w/\overline{M}_n$ was 1.18; the percentages of isotactic and heterotactic triads were 99 (I) and 1 (H). The value of $\overline{M}_w$ for the syndiotactic fraction was 2.15×10^5 and $\overline{M}_w/\overline{M}_n$ was 1.37; the percentages of isotactic, syndiotactic and heterotactic triads were 2 (I), 74 (S) and 24 (H).

Electron Microscopy. Solutions of isotactic and syndiotactic PMMA were first made up separately in tetrahydrofuran; the concentrations were 4×10^{-4} and 16×10^{-4} g/cm^3 respectively. Equal volumes of these two solutions were then thoroughly mixed in a flask thermostatted at 20°C. Complex formation between the isotactic and syndiotactic polymers (in the ratio 1:4 by weight) was followed by removing small drops of solution from the flask at various times. Immediately after removal, the drops were allowed to spread and dry on a carbon substrate supported by a copper grid. Electron micrographs were obtained of the dried polymer specimens using a JEOL 100CX electron microscope operating at 80 kV. During the drying process, some distortion of the structures formed by the stereocomplexes in solution would have occurred. The nature of the structures observed by electron microscopy and their reproducibility however indicated that the technique could provide a useful semiquantitative guide to the processes occurring in solution.

RESULTS

The electron micrographs indicate that, in the early stages of complex formation between the two polymers, globular particles were formed in solution as shown in Figure 1. The majority of particles in the dried state have sizes ranging from 100 to 200 nm. Earlier light scattering studies on a similar system by Katime and Quintana (18) revealed globular particles with dimensions of the same order of magnitude.

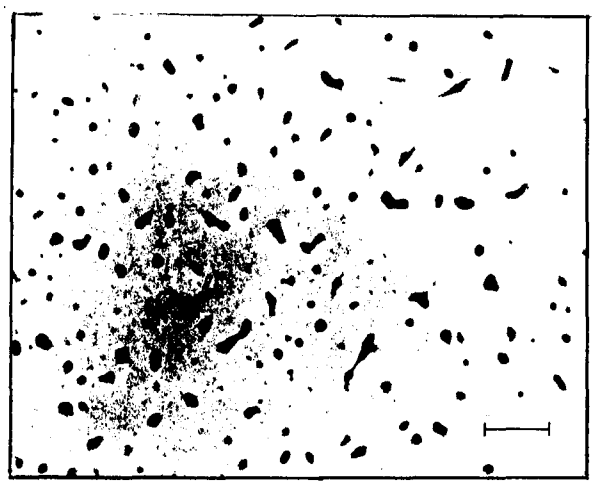

Figure 1. Electron micrograph of stereocomplex particles isolated from solution 2 hours after mixing. Scale bar is 2 μm.

Specimens isolated from solution after longer periods showed branched fibrillar particles as shown in Figures 2 and 3. Such observations are in partial agreement with the results of Mekenitskaya et al. (22) who, as a result of solution studies, suggested that the stereocomplex particles were rod shaped.

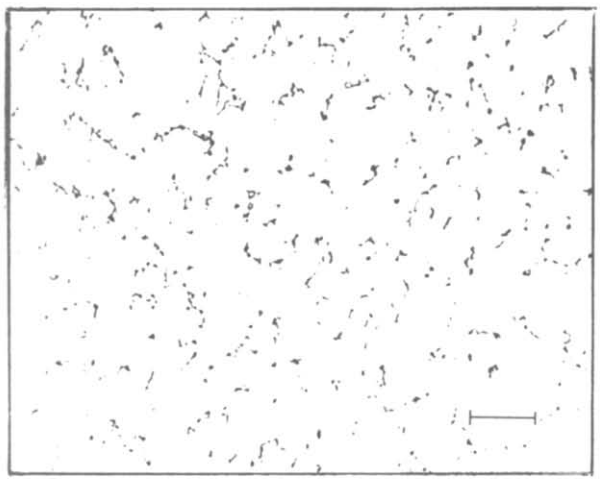

Figure 2. Electron micrograph of stereocomplex particles isolated from solution 49 hours after mixing. Scale bar is 5 μm.

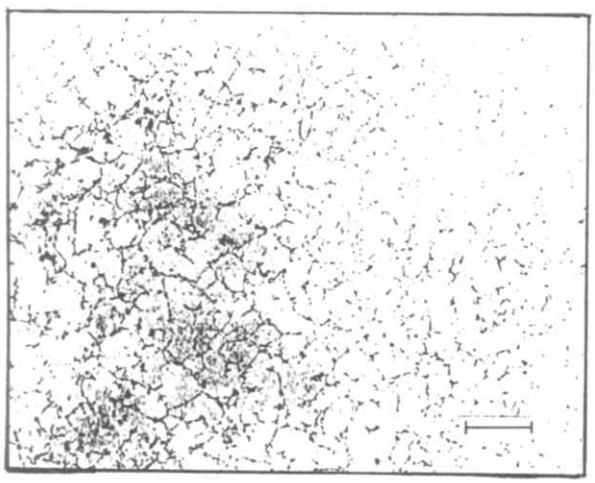

Figure 3. Electron micrograph of branched stereocomplex particles isolated from solution 146 hours after mixing. Scale bar is 5 μm.

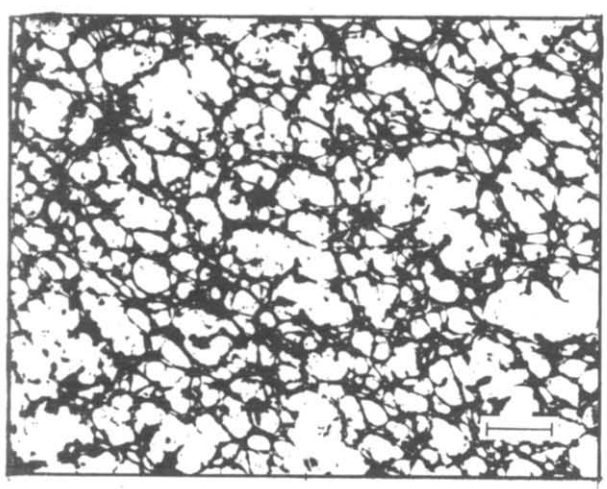

Figure 4. Electron micrograph of polymer specimen isolated from solution 584 hours after mixing, showing evidence of network formation. Scale bar is 2 μm.

Eventually in the later stages of complex formation, as shown in Figure 4, an open network is formed, consistent with the presence of microgel in such systems.

Complex formation between the isotactic and syndiotactic samples of PMMA in tetrahydrofuran was also studied by electron microscopy at a 1:1 ratio of polymers. Similar electron micrographs were observed as for the 1:4 ratio, leading to the formation of network structures. As reported earlier (18) however, for polymers with the tacticities used in the present study, the optimum ratio for complex formation is 1:4.

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