Associations of stereoregular polymethylmethacrylates

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This thesis describes the association of stereoregular poly(methyl metha-
crylates) in dilute solutions and in bulk. It is known that isotactic and
syndiotactic poly(methyl methacrylate) (i- and s-PMMA) have complementary
structures and that specific interactions occur between i- and s-PMMA
(Chapter 1).

Stereocomplex formation of i- and s-PMMA can take place in dilute so-
lutions far below the homogeneous segmental distribution concentration,
which was demonstrated by means of viscometric and turbidimetric measure-
ments. As the solvent appeared to influence considerably the degree of
association, an empirical division was made into 3 groups: A - strongly
complexing solvents (e.g. acetone, DMF, DMSO, acetonitrile, methyl iso-
butyrate and monomer MMA); B - weakly complexing solvents (e.g. toluene
and benzene); C - non-complexing solvents (e.g. chloroform) (Chapter 2).
The tacticity of s-PMMA appears to influence the association process
strongly whereas a narrower molecular weight distribution of i-PMMA has
only little influence (Appendix 1).

Based upon the results of differential scanning calorimetry (d.s.c.)
and X-ray powder diffraction patterns we conclude that in dilute type
A solutions i- and s-PMMA chains partly associate in an i/s ratio of
about 1:1 and that at the same time liquid induced crystallization of s-
PMMA occurs (Chapter 3).

Thermal analysis showed that material associated in dilute type A solu-
tions had 3 endotherms at temperatures not depending on the composition
of the sample. The endotherm at $\approx 210^{o}$C is caused by the melting of the
stereocomplex, the endotherm at $\approx 185^{o}$C by the melting of solvent sta-
bilized s-PMMA, while the endotherm at $\approx 280^{o}$C is caused by the degra-
dation of PMMA (Chapter 3).

Association of i- and s-PMMA can also occur in bulk as demonstrated
by means of calorimetric and dynamic - mechanical measurements. The rate
of complex formation is maximal at 140°C and the extent of complex for-
mation is maximal at a composition somewhat lower than the i/s ratio of

1:1. The high rate of complex formation in bulk - more than half of the complex has been formed within 2 minutes at 140°C - is remarkable the more so as the separate components do not crystallize at all under these conditions (Chapter 4).

As mechanism for complex formation in bulk it is proposed that chain segments of i-PMMA form nuclei by adopting the favourable 5_1 helix conformation, whereupon chain segments of s-PMMA associate with these favourable places yielding a fringed micelle like structure. As the association continues the crystalline regions are extended appearing from the fact that annealed and non-annealed samples had about the same value of the storage modulus (G') above the glass transition temperature (Chapter 4).

In order to compare the properties of the stereocomplex with those of pure i- and s-PMMA, the crystallization of i- and s-PMMA was studied. i-PMMA is a very slowly crystallizing polymer with a maximal growth rate ($G = 1 \times 10^{-3}$ µm/min) of the crystals at 120°C, while the estimated (equilibrium) melting temperature (T_m^o) is 220°C (Chapter 5). The crystallization of s-PMMA from the melt appeared to be even more troublesome. Therefore s-PMMA was treated with borderline solvents (heptanone-4, methyl isobutyrate and toluene). This material which had not been fully dried, showed an endotherm at $\approx 190^{\circ}$C as recorded by d.s.c. and a reflection at $2\theta = 4^{\circ}30'$ in the X-ray diffractogram. Drying the sample further resulted in the disappearance of endotherm and reflection. From this it may be concluded that some crystalline structure of s-PMMA is stabilized by solvent (Appendix 2).

IR spectroscopy showed that upon complex formation in dilute type A solutions s-PMMA mostly takes on a planar structure with a glide plane, whereas i-PMMA has a 5_1 helix conformation in the stereocomplex and that association of i- and s-PMMA occurs over long distances along the chains. Preliminary fibre diffraction measurements showed that the c axis of the unit cell of the stereocomplex is ≈ 1 Å shorter than that of i-PMMA (Chapter 6).

The difference in configuration and conformation of i- and s-PMMA also appeared to influence the mixing behaviour of PMMA and PVC [poly(vinylchloride)] . i-PMMA and PVC form an incompatible system, whereas s-PMMA and PVC form a compatible system up to a composition corresponding with a monomer unit ratio of 1:1 (PVC : s-PMMA) (Chapter 7).