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"Stereocomplex" Formation and an Antipathic Behavior between Isotactic and Conventional Polymethyl Methacrylate

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LETTER TO THE EDITOR

"Stereocomplex" Formation and an Antipathic Behavior between Isotactic and Conventional Polymethyl Methacrylate

We have recently found a characteristic phenomenon of polymethyl methacrylate in acetone solutions: if a sufficiently high (>1%) concentrated acetone solution of isotactic polymethyl methacrylate is mixed with a similar acetone solution of conventional ("atactic") polymethyl methacrylate, the turbidity increases and a gel-like structure forms.

This phenomenon is very similar to that reported by Liquori et al. [1] and some other groups [2] on stereocomplex formation between isotactic and syndiotactic polymethyl methacrylates in polar solvents. It should be noted that, in our case, the "stereocomplex" formation takes place between isotactic and conventional polymethyl methacrylate in acetone solutions, and that the resultant structure demonstrates thermally reversible sol-gel transformation. The transition temperature depends on the composition, but lies invariably below the boiling point of acetone. At the boiling temperature, almost all of the gels transform into clear solutions.

Another important phenomenon is found if isotactic and conventional polymethyl methacrylates are combined in acetone solutions. If solid isotactic polymethyl methacrylate (freeze-dried from benzene solution) is added to an acetone solution of conventional polymethyl methacrylate, turbid sols appear at room temperature but clear solutions appear at higher temperatures.

If solid conventional polymethyl methacrylate (freeze-dried from benzene solution) is added to an acetone solution of isotactic polymethyl methacrylate, the conventional polymethyl methacrylate only swells, even at the boiling temperature of acetone. The isotactic polymethyl methacrylate-acetone solution is therefore losing its dissolving power and behaves just like a saturated solu-

tion of low molecular weight compounds for the conventional polymethyl methacrylate. This behavior was not observed in benzene and chloroform solutions.

This type of antipathic behavior has not been observed in studies of synthetic polymers. Some analogous phenomena have been observed in natural polymers, however. The synthetic polymers may thus be used as interesting models for the investigation of specific interactions in biopolymer systems as well as in the systems reported so far [1, 2]. A systematic investigation is now in progress.

The following two different polymer samples were used in this preliminary work.

Isotactic polymethyl methacrylate was prepared by anionic polymerization of methyl methacrylate monomer initiated with $LiAlH_4$/ethyl ether system at Dry Ice/acetone temperature for 16 hr and purified by fractional precipitation from a benzene/n-hexane mixture. Code number: (5)-2; $\bar{M}_V = 5.7 \times 10^5$. The isotactic fraction of the polymer (more than 90% of the total) contained more than 90% isotactic triads as determined by NMR.

A conventional polymethyl methacrylate was prepared by bulk polymerization of methyl methacrylate monomer at 60°C initiated by azobisisobutyronitrile and purified by fractional precipitation from an acetone/water mixture (about 60% recovery). Code number: (A1); $\bar{M}_V = 2.2 \times 10^5$. This sample contained 11.8% isotactic, 27.3% heterotactic, and 60.9% syndiotactic triads (NMR).

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