

## Stereocomplex Formation of Atactic Poly(methyl methacrylate)

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**Abstract:** Stereocomplexes formed in atactic poly(methyl methacrylate) (*a*-PMMA) films cast from different solvents were studied by means of Fourier transform infrared spectroscopy (FTIR), and differential scanning calorimetry (DSC). The growth of stereocomplex was a function of annealing temperature and annealing time, respectively.

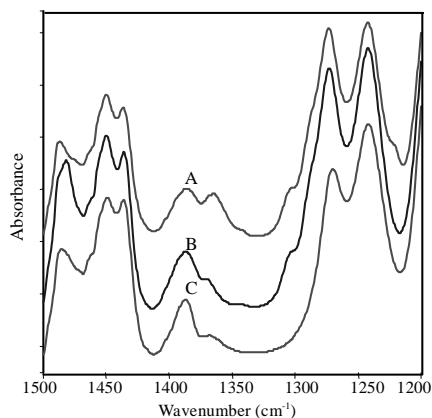
**Keywords:** Atactic poly(methyl methacrylate), stereocomplex, annealing.

It has been known that mixing of syndiotactic and isotactic poly (methyl methacrylate) (PMMA) copolymers in some suitable solvents can form stereocomplexes by the van der Waals force between the syndiotactic and isotactic segments<sup>1</sup>, but whether stereocomplex could be formed in *a*-PMMA has been still a puzzle<sup>2-4</sup>. In this paper, we wish to find out whether *a*-PMMA could form stereocomplexes, and the relationship between stereocomplexation and annealing conditions was also discussed.

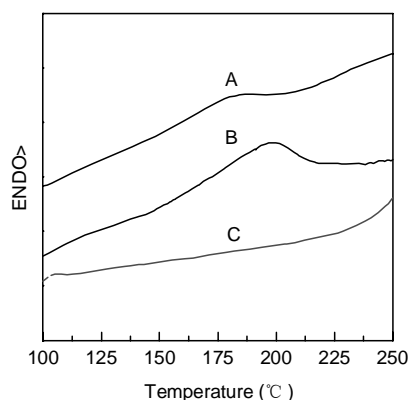
FTIR spectra of the *a*-PMMA films, prepared by cast from acetone, benzene and chloroform solutions, were measured by using Perkin-Elmer FTIR 2000 spectrometer. The as-cast films and those cast from acetone annealed under different annealing conditions were scanned by using TA-2910 DSC with the scan speed of 40°C/min.

It is known that acetone, benzene, and chloroform are distinguished into strongly,

**Figure 1** FTIR spectra of *a*-PMMA film cast from different solvents A: acetone; B: benzene; C: chloroform.



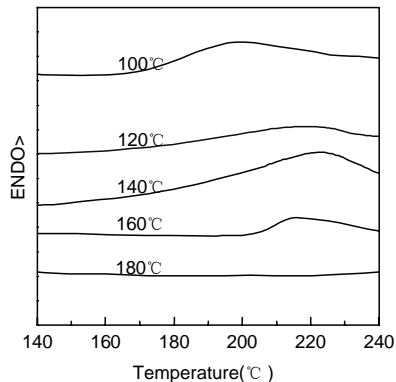
**Figure 2** DSC heating scans of *a*-PMMA films cast from solvents A: acetone; B: benzene; C: chloroform.



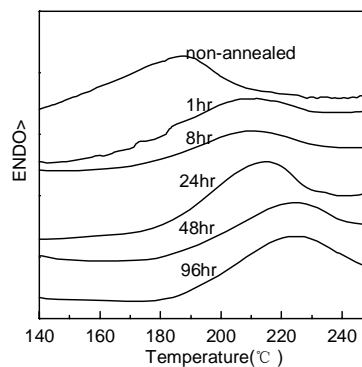
weakly, and nonstereocomplexing solvents, respectively<sup>5</sup>. **Figure 1** shows that the intensities of bands at  $1270\text{cm}^{-1}$  and  $1450\text{cm}^{-1}$  of films increase in accordance with the increase of stereocomplexation capability of solvents. The former corresponds to *trans-trans* conformation of the backbone<sup>6</sup>, and the latter corresponds to *cis* and *trans* conformation of the side chain<sup>7</sup>. The increases of the population of these conformers mean the formation of ordered structure, *i. e.* stereocomplex, in films cast from acetone and benzene. In addition, an endotherm was observed only for the two films (see **Figure 2**). It demonstrated that stereocomplexes actually formed and the endotherm is ascribed to the melting of the structure<sup>8</sup>.

Moreover, the dependence of stereocomplex growth on annealing temperature ( $T_a$ ), annealing time ( $t_a$ ) was studied for films cast from acetone. With the increase of  $T_a$  the endotherm shifts to higher temperature and reaches maximum at  $140^\circ\text{C}$  (see **Figure 3**). The endotherm dependence on  $T_a$  implied that much larger size and stable ordered domains were formed at higher  $T_a$ <sup>9</sup>. While  $T_a$  is over  $140^\circ\text{C}$  the endotherm declines and disappears at  $180^\circ\text{C}$ . It indicated that the ordered structures formed in the solutions became imperfect and their number decreased at higher  $T_a$ . Besides, when  $T_a$  remains with the increase of  $t_a$  the endotherm also shifts to higher temperature and goes through

**Figure 3** DSC curves *a*-PMMA of film cast from acetone annealed for 24hr at indicated temperatures



**Figure 4** DSC curves of *a*-PMMA film cast from acetone annealed at  $140^\circ\text{C}$  for different time



maximum when  $t_a$  is 48 hr (see **Figure 4**), which is probably due to the rearrangement and perfection of the ordered structures.

## References

1. T. G. Fox, B. S. Goode, W. E. Gratch *et al.*, *J. Am. Chem. Soc.*, **1958**, *80*, 1768.
2. W. Borchard, M. Pyrik, G. Rehage, *Makromol Chem.*, **1971**, *145*, 169.
3. A. Horta, M. G. Prolongo, R. M. Masegosa *et al.*, *Polymer*, **1981**, *22*, 1147.
4. J. Spevacek, I. Fernandez-Pierola, *Makromol. Chem.*, **1987**, *188*, 861.
5. G. Challa, A. de Boer, Y. Y. Tan, *Int. J. Polym. Mat.*, **1976**, *4*, 239.
6. L. Lipschitz, *Polym. Plast. Technol. Eng.*, **1982**, *19*, 53.
7. J. Dybal, J. Stokr, B. Schneider, *Polymer*, **1983**, *24*, 971.
8. A. de Boer, G. Challa, *Polymer*, **1976**, *17*, 633.
9. E. Schomaker, G. Challa, *Macromolecules*, **1988**, *21*, 2195.

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