Stereocomplex formation in atactic poly(methyl methacrylate)
I. Effect of solvents

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Summary

The stereocomplexation in three kinds of atactic poly (methyl methacrylate) (*a*-PMMA) films with different tacticities isolated from acetone, benzene, and chloroform solution was studied by Fourier transformation infrared (FTIR) and differential calorimetry scanning (DSC) techniques. Based on the results of infrared spectra, it could be deduced that stereocomplexes were formed in the films cast from acetone and benzene solutions with the increase in the population of *trans-trans* (*tt*) conformation of the backbone of *i*- and *s*-segments. It was assumed that the stereocomplexes formed by the interactions between *i*- and *s*-segments, possibly including intramolecular complexation. The stereocomplexation was also confirmed by the evidence of a endotherm with melt temperature over the range 180°C to 200°C, which was corresponded to the melting stereocomplex aggregates formed in the solutions and stabilized by the solvent molecules.

Introduction

It has been known that in some solvents, mixing of the solution of isotactic poly(methyl methacrylate) (*i*-PMMA) and syndiotactic poly(methyl methacrylate) (*s*-PMMA) leads to form a crystalline polymer-polymer aggregates called stereocomplex (1-2). Stereocomplex formation is supposed to take place in consequence of mutual interactions of the ester groups of *i*- and *s*-PMMA (3), or in consequence of interactions of *i*-PMMA ester groups with α-CH$_3$ groups of the syndiotactic component (4-5). It is found that the solvent used has a considerable influence on complex formation so that solvents for PMMA can be divided into three groups: those strongly complexing (e.g. acetone, tetrahydrofuran); those weakly complexing (e.g. benzene, toluene); and others non-complexing (e.g. chloroform, dichloromethane) (6). Others factors, such as molecular weight, polymer concentration, mix ratio of the stereoregular polymers, complexation time, complexation temperature and stereosegment lengths, must also be taken into account (7-9).

The PMMA chains forms helical structures in the stereocomplex, which is analogous to the structures of biological polymers, and the stereocomplex formation strongly affects the properties of PMMA. Researches on the stereocomplexation have been focused mainly on homopolymer blends, and the blends of *i*-PMMA and several syndiotactic polymethacrylates (10, 11). Recently, complex formation in blends of *i*-PMMA and *s*-copolymers of methyl metharyalte and alkyl methacrylates has been reported (12-16).

As for atactic poly(methyl methacrylate) (*a*-PMMA) whether it can form stereocomplex in solutions or bulk has been still in problem. Measurements of flow birefringence of PMMA of stereoblock structure (I=46%; H=28%; S=33%) in toluene solution indicate the presence of organized structures ascribed to interactions of *i*- and *s*-segments of the same molecule (17). Borchard *et al*. (18-19) have observed a maximum in the temperature dependence of η_{SP}/c, as well as an anomalous concentration

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dependence in toluene which is explained by intramolecular association of short *i*- and *s*-segments by interactions of stereocomplex type. In addition to papers findings aggregation at *a*-PMMA in toluene (18-20), there also exists papers claiming no aggregation (21-22). Recently, Spevacek *et al* (23) have proved the stereocomplexation of heterotactic-PMMA (*h*-PMMA) in some solutions by using NMR.

The presentation paper gave the results of researches on stereocomplexation in *a*-PMMA with different tacticities by means of FTIR and DSC. Stereocomplex was found in the three samples when cast from strongly and weakly complexing solvents i.e. acetone and benzene, respectively.

Experimental

Samples Three kinds of *a*-PMMA samples were kindly supplied by Dong Zhang Chemical Factory, Jiangsu province. The tacticities of the three samples determined by ^{1}H NMR were listed in Table 1.

Table 1 Characterization of the samples of *a*-PMMA

Samples	Tacticity (%)			Average segment lengths (monomer unit)	
	mm	mr	rr	mm	rr
I	6.8	41.7	51.5	1.33	3.47
II	7.7	37.3	55	1.41	3.95
III	9	34	57	1.53	4.35

FTIR Spectrum measurements The infrared spectra were recorded on PE-FTIR 2000 system spectrometer. *a*-PMMA powder was dissolved in acetone, benzene, and chloroform, then cast onto a NaCl plate respectively. After the solvent was evaporated, spectra were obtained at room temperature.

DSC measurements *a*-PMMA samples were prepared by casting their 5 wt% acetone, benzene, and chloroform solutions onto glass plate, then the films were dried in a vacuum oven at room temperature in order to vaporize the solvents. Differential scanning calorimetry (DSC) measurements were conducted with a TA 2910 instrument calibrated with ultrapure indium. Scans were made at a heating rate of 40 °C/min. The melting temperatures T_m were recorded corresponding to the peak of the endotherm.

Results and discussion

In the IR spectrum of the films of sample I cast from different solutions, there appear differences at the wavenumber range 860 cm^{-1} and 954 cm^{-1} as shown in figure 1(a) and 1(b). Two weakly shoulder bands appear there only for the film cast from acetone and benzene solutions, respectively. Moreover, the intensities of the two shoulder bands decrease in the order of from acetone to benzene.

It is reported that the intensities of the doublet at 843 and 860 cm^{-1} are sensitive to the conformational structure of *s*-PMMA. The formation of the stereocomplex is manifested by an increase in the intensity of the band at 860 cm^{-1} (24). So the appearance of band 860cm^{-1} indicated that stereocomplex formed, and the conformational structure of *s*-segments was changed, which was in the extended chain form with the energetically favored *tt* conformation of the carbon backbone. In comparison with non-aggregated amorphous *s*-segments where *tt* conformational forms also dominate the extended chain conformation of *s*-segments in stereocomplex persists over longer distance.

It has been reported that the structure of *i*-PMMA crystal should be also in the double helical structure, i. e. in a conformation deviating only slightly from the extended chain

form, which is characterized by the band at 954 cm^{-1} (25-27). Schneider *et al.* further states that the *i*-PMMA chains in the stereocomplex have the similar conformational structure as in the crystalline *i*-PMMA (28). Therefore the appearance of shoulder band 954 cm^{-1} indicated that part of *i*-segments was in *tt* conformation and took part in formation stereocomplex.
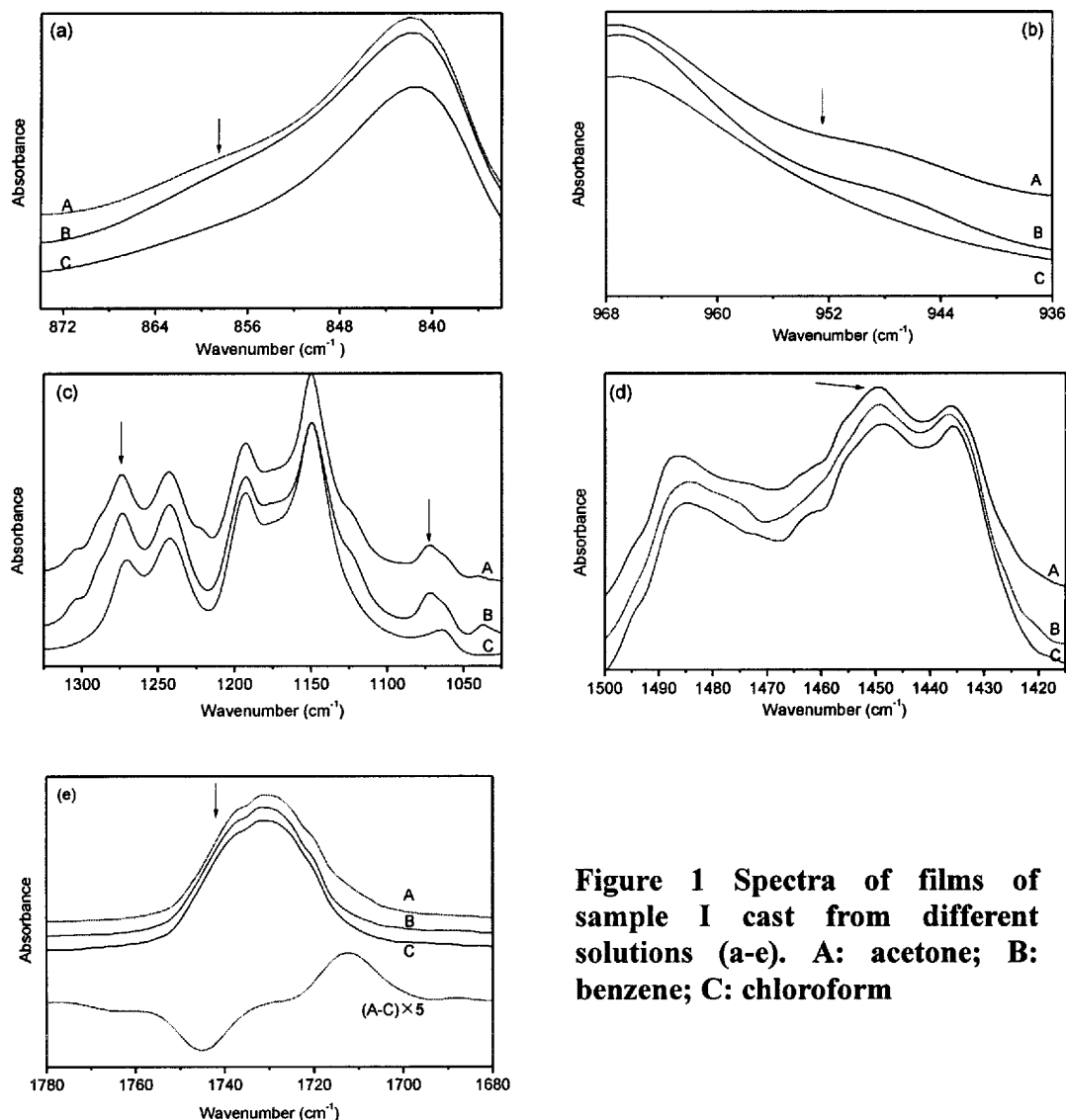

Figure 1 Spectra of films of sample I cast from different solutions (a-e). A: acetone; B: benzene; C: chloroform

The band at 1276cm^{-1} could be assigned to a backbone conformation, namely *tt* conformation, for the hydrogenous polymer (29). As to *a*-PMMA the band at 1270 cm^{-1} is assigned to the planar zigzag arrangement of backbone carbon atoms (30). As shown in figure 1(c), the intensities of the band increased according to the solvents' ability for complexing, which indicated that more *a*-PMMA backbone chains in films cast from acetone and benzene solutions were in *tt* conformation than those cast from chloroform solution. In other word, the local regularity of chains was increased in strongly and weakly complexing solvent.

With the change of conformation of the backbone chain side-chains also had to adjust their conformation because of the effect of internal energy and steric hindrance. The band at 1450 cm^{-1} corresponds to the antisymmetrical bending vibration of the group $O(CH_3)$

(31). Schneider *et al.*(24) have assumed that the band at 1450 cm^{-1} for *s*-PMMA corresponds to the energetically most favored conformational structure of ester group, which means that the bonds C=O and C-CH$_3$ are in mutual *cis* orientation, while for *i*-PMMA only *cis* and *trans* structures of the ester groups are present when the backbone chains are in *tt* conformation because the occurrence of *gauche* structures is limited by steric hindrance. Shown by figure 1(d), the intensity ratio of band at 1450 cm^{-1} to that at 1438 cm^{-1} also increases with the increase in the complexation ability of the solvents. Namely, more population of ester groups in *a*-PMMA were in *cis* and *trans* conformations with the increase in the population of the *tt* conformation of the backbone chains. So in order to form the stereocomplex the *s*-segments and *i*-segments should be in the state of extended chain, namely, the carbon backbone was in an approximate *tt* conformation with the ester groups of *s*-segments in *cis* and those of *i*-segments alternating in *cis* and *trans* orientation, respectively.

It was noteworthy to pay an attention to the wavenumber shift of the band at 1063cm^{-1}, which is ascribed to the intramolecular interaction (30). That the band shifts to higher wavenumber means the intensification of the intramolecular interactions with the increase in complexing ability of the solvent, which possibly resulted from the stereocomplexation. Hatada *et al*. report that the direct chemical bond linking of uniform *i*- and *s*-sequence in stereoblock PMMA makes the complex formation more easier than that in the case of between *i*-PMMA and *s*-PMMA (15, 16). They also find direct evidence of formation of intramolecular and intermolecular stereocomplexes in stereoblock PMMA (32, 33). So it maybe assumed that the stereocomplexes were formed partly by the interactions between the *i*- and *s*-segments of the same chain based on our results of ir spectrum, which was also in accordance with the assumption proposed in ref. 17.

Moreover, it is well known that in the stereocomplexation process two mechanisms are possible, i. e. mutual interaction of *i*- and *s*-segments (stereocomplex type) and mutual interaction of *s*-segments (*s*-PMMA self-aggregation type). Self-aggregation in *s*-PMMA is manifested in ir spectra by the appearance of a new band at 1742cm^{-1}, while in the case of PMMA stereocomplex a single symmetrical band at 1731 cm^{-1} is observed (34). In the IR spectra and their difference spectrum (see in figure 1(e)) the band 1742 cm^{-1} was not observed either. Therefore, we assumed that stereocomplexation of *a*-PMMA was caused by interactions of stereocomplex type similarly to the aggregation mechanism of *h*-PMMA (23).

The IR spectra of films of sample II and sample III cast from different solutions were shown in figure 2. The variation tendencies of bands labeled by arrows were in a similar way to those discussed above for sample I. So it could be assumed that stereocomplex also formed in sample II and sample III.

Thermal behaviors of all the three samples isolated from acetone, benzene and chloroform solutions were shown in figure 3. A melting
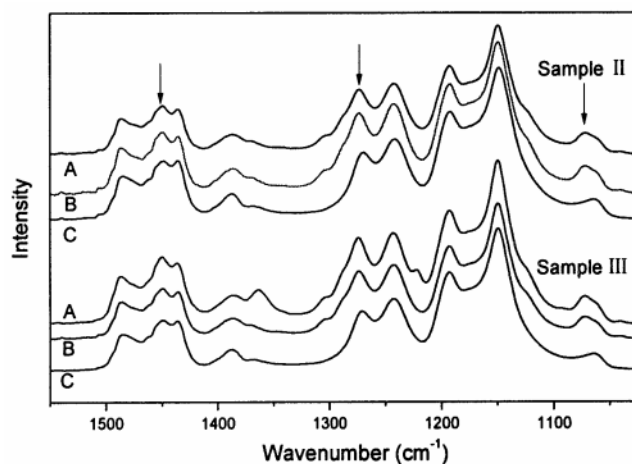

Figure 2 Spectra of films of sample II and sample III cast from different solutions. A: acetone; B: benzene; C: chloroform

endotherm with melt temperature about 180°C to 200°C was observed for all the three samples cast from acetone and benzene solutions. This endotherm was attributable to the solvent stabilized crystalline-like segments in complexing solvent consisting of compact and stable nuclei surrounded by a shell of noncompelxed chains (9, 35). The results also confirmed that stereocomplexes actually formed in *a*-PMMA with different tacticities. Meanwhile, it is found that the melting endotherm for stereocomplexes formed in benzene solution is broader and more pointless than that formed in acetone solution, but its melting temperature is slightly higher. For the stereocomplex formation, one of the decisive factors is the stereoregularity of polymer chains. Therefore a stable ordered structure be formed only in those cases where the length of the interacting segments is longer than some minimum. The actual values of this minimum length depend on the solvent: in the case of strongly complexing solvent the minimum length of associated *s*-segments is 3-4 monomer, and weakly complexing is 10 (36, 37). So it was assumed that the stereocomplexes formed in benzene solution were in larger size, but were imperfect in the structure in comparison with those formed in acetone solution based on their thermal behaviors.
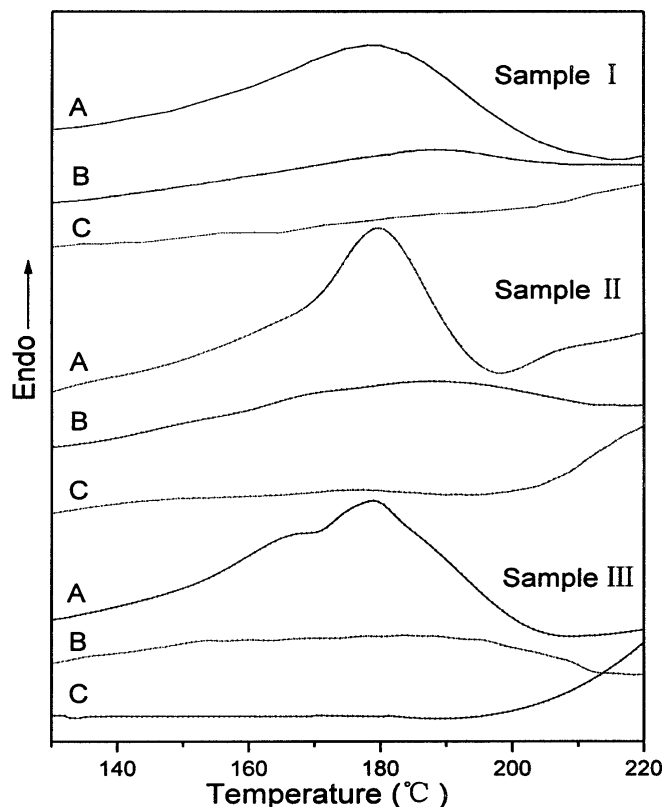

Figure 3 Spectra of films of sample II and sample III cast from different solutions. A: acetone; B: benzene; C: chloroform

Conclusions

Stereocomplex formed in the *a*-PMMA films cast from acetone and benzene solutions approved by the results of FTIR and DSC researches. The population of *trans-trans* conformers of the *a*-PMMA backbone chains increased with stereocomplexation. The intramolecular interactions between the s- and *i*-segments of the same polymer chain may be play a part role in the process of stereocomplexation.

Acknowledgments

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