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PMMA 的立體異構性對它和另一高分子相容性的影響

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計畫主持人：徐文平　博士

執行單位：嘉南藥理科技大學　醫藥化學系

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SYNOPSIS

Isotactic, atactic and syndiotactic poly (methyl methacrylates) (PMMAs) (designated as iPMMA, aPMMA and sPMMA) with approximately the same molecular weight were mixed separately with poly (vinyl pyrrolidone) (abbreviated as PVP) mostly in chloroform to make three polymer blend systems. Differential scanning calorimetry (DSC) was used to study the miscibility of these blends. The results showed that the tacticity of PMMA has a definite impact on its miscibility with PVP. The aPMMA/PVP and sPMMA/PVP blends were found to be miscible because all the prepared films showed composition dependent glass transition temperatures (T_gs). The glass transition temperatures of the aPMMA/PVP blends are equal to or lower than weight average and can be qualitatively described by the Gordon-Taylor equation. The glass transition temperatures of the other miscible blends (i.e. sPMMA/PVP blends) are mostly higher than weight average and can be approximately fitted by the simplified Kwei equation. The iPMMA/PVP blends were found to be immiscible or partially miscible based on the observation of two glass transition temperatures. The immiscibility is probably caused by stronger interaction among isotactic MMA segments due to the fact that its ordination and molecular packing contributing to form a rigid domain.

INTRODUCTION

It has been known for years that the stereoregularity of polymer chains influences polymer-polymer miscibility. Due to its availability in both syndiotactic and isotactic forms, poly (methyl methacrylate) (PMMA) has been used frequently in the investigation of the effect of tacticity on miscibility. Several papers[1-8] have shown that the tacticity of PMMA influences blend compatibility, when PMMA is blended with a chemically different polymer. Because of differences in the molecular weights and the preparation methods of the samples, the results sometimes are not consistent. Since atactic PMMA is mainly composed of syndiotactic one, the result of atactic one is often similar to syndiotactic one.

Most of the previous studies[1-8] were concentrated on few blends such as poly (vinylidene fluoride) (PVDF), poly (ethylene oxide) (PEO) and poly (vinyl chloride) (PVC) with stereoregular PMMA. However, few studies were focused on other polymers blended with stereoregular PMMA. Recently da Silva and Tavares[9] investigated the behavior of poly (methyl methacrylate)/poly (vinyl pyrrolidone) (PMMA/PVP) blends by solid state nuclear magnetic resonance (NMR) using proton spin-lattice relaxation time in the rotating frame ($T_1^H{}_\rho$). Based on their observation, miscibility was detected for all the proportions studied as a consequence of the interaction process of blend components.

Poly (vinyl pyrrolidone) (PVP) is a water soluble tertiary amide and a strong lewis base. As a result, it is susceptible to form hydrogen bonds with substances containing hydrogen donor groups. It has been shown to form a large number of polymers such as poly (vinyl chloride) and poly (epichlorohydrin)[10], poly (vinyl fluoride)[11], poly (2-hydroxyethyl methacrylate)[12], poly (hydroxy ether of bisphenol A)[13] and poly (vinyl phenol)[14]. Not surprisingly, PMMA has shown to be miscible or partially miscible with those polymers aforementioned miscible with PVP.

Motivated by the results of da Silva et al.[9] and also to our knowledge there have been no reports about tacticity effect of PMMA on the miscibility with PVP. Based on their results[9], it is concluded that aPMMA is miscible with PVP. Although they didn't specify the tacticity of PMMA, the commercial PMMA is often considered to be atactic. Therefore, a systematic study of

the effect of tacticity of PMMA on its miscibility with PVP is worthwhile and was pursued in our laboratory.

In this article, isotactic, atactic and syndiotactic PMMAs with approximately the same molecular weight were blended with PVP mostly in chloroform to cast into films. The glass transition temperatures of the polymers were measured calorimetrically. In this report, the miscibility of the prepared blends is investigated based on the data of glass transition temperatures.

EXPERIMENTAL

Materials and Film Preparation

Isotactic , atactic and syndiotactic PMMAs (designated as i, a and sPMMA in this study) were purchased from Polysciences, Inc., Warrington, PA. According to the supplier information, the molecular weights (M_ws) of iPMMA, aPMMA and sPMMA are the same about 100,000 g/mol. The polydispersities (M_w/M_n) of the three PMMAs were not measured therefore not reported here. However, the molecular weight distribution effect is believed to be minimal in the current study when compared with the effect of tacticity. We didn't characterize the tacticity of PMMA by NMR. Therefore, a simple estimation of the fractions of meso (m) and racemic (r) diads was resorted. The meso diad fractions of PMMA were computed previously[15] and are listed in Table I. Validation of the estimation is proven by comparing the m and r fractions of aPMMA with Li and Brisson's data[16]. They used the same molecular weight aPMMA from Polysciences. In their report, they characterized the tacticity of aPMMA to be 16% isotactic, 45% heterotactic and 39% syndiotactic. When converted to m and r fractions(also listed in Table I), m fraction (%) = 16+45/2 = 38.5 and r fraction(%) = 39+45/2 = 61.5. Our computed m and r values (33.8% and 66.5%) are in agreement with theirs within the error of estimation.

Two different sources of PVP were used to blend with PMMA. PVP1 was obtained from Riedel-de Haën Germany laboratory chemicals and had an M_v value about 10,000 g/mol. PVP2 was purchased from Aldrich Chemical Company Inc., Milwaukee, WI and its M_w value is 55,000 g/mol. PVP1 or PVP2 was mixed with each tactic PMMA individually in chloroform at room temperature in several weight ratios to form blends.

Thin films of individual polymers and their blends were made by solution casting onto glass plates. Chloroform was used as solvent, but for PMMA toluene was used instead. Chloroform and toluene are all A.C.S. reagents purchased from Fisher Scientific, Fair Lawn, N.J. The final drying step for all the films took place in a vacuum oven for about 16 hrs at 92-155 ℃, which was above the glass transition temperatures of the individual polymers. Then the films were cooled down to room temperature slowly by air. The as-cast films were later used for DSC studies. The applied drying and vacuuming conditions were proven to be enough for eliminating all residual solvent since no solvent peak detected by DSC.

Differential Scanning Calorimetry (DSC)

The glass transition temperatures (T_gs) of the polymer blends were determined by using a DuPont 2000 thermal analyzer with an accessory of mechanical cooling system. Experiments were performed in two consecutive scans in an ambient environment of nitrogen gas at a flowing rate of 100-110 ml/min. In the end of the first thermal scan, the samples stayed at 220℃ for 1 min. Then the samples were cooled to 20℃ at a rate of 20℃/min and were scanned a second time. A scanning temperature from 20 to 220℃ and a heating rate of 20℃/min were used in each scan. The inflection point of the specific heat jump of the second thermal scan was taken as the glass transition temperature. Although our previous publication[15] used an ice-water bath in the end of the first thermal scan to obtain T_g of the quenched samples. The cooling rate of 20℃/min used in this study produced almost the same T_g as quenching within experimental error.

RESULTS AND DISCUSSION

Since the majority of solvent used was chloroform and only in one blend system THF was used additionally for comparison.

Therefore, when no solvent name was referred in this section it is considered to be chloroform. However, it will be denoted clearly when THF was used as the solvent.

Glass Transition Temperature

The T_g values of three tactic PMMA/PVP1 blends are listed in Table II. For the aPMMA/PVP1 and sPMMA/PVP1 blends, only one T_g was detected for each blend composition. It can be concluded that these two blends are miscible based on a single T_g criterion. Although T_gs of aPMMA, sPMMA and PVP1 are at most 16℃ apart, based on their T_g behavior their miscibility is certain. However, two T_gs were observed in the iPMMA/PVP1 blends. Therefore the iPMMA/PVP1 blends are determined to be partially miscible because of phase separation and also due to the fact that T_g values are located between those of the component polymers. Table III shows the result of PMMA/PVP2 blends. The data of Table III bear out similar conclusion as Table II. The aPMMA/PVP2 and sPMMA/PVP2 blends are miscible, however, immiscibility was mostly found between iPMMA and PVP2. For a high PVP2 composition (75.1%), the blend showed partial miscibility on account of the observation of low T_g higher than iPMMA's T_g and high T_g even higher than that of PVP2. The glass transition temperature regions (ΔT_g) were calculated as differences between the onset and end points of T_g. All the ΔT_g values of the blends are listed in Tables II and III for reference. For miscible aPMMA/PVP1 (or 2) and sPMMA/PVP1 (or 2) blends no or little broadening of the glass transition temperature was detected.

CONCLUSIONS

The results show that the backbone conformation of PMMA plays a major role in its miscibility with PVP. The prepared aPMMA/PVP1 (or PVP2) and sPMMA/PVP1 (PVP2) blends are determined to be miscible based on a single glass transition temperature for each composition of the films. Conversely, iPMMA is immiscible or partially miscible with PVP1 (or PVP2) because of the observation of two glass transition temperatures in all the studied blends.

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Table I Meso and racemic fractions of tactic PMMA

	m (%)	r (%)
iPMMA	68.7	31.3
aPMMA	33.8	66.2
aPMMA[a]	38.5	61.5
sPMMA	9.3	90.7

*error of estimation= 5-8%

[a]taken from reference 16

Table II Glass transition temperatures of chloroform-cast PMMA/PVP1 blends

	T_g (℃)	ΔTg (℃)
(1) iPMMA/PVP1		
100/0	74.6	20
87.7/12.3	76.8, 119.8	12, 14
74.5/25.5	79.5, 115.0	16, 13
50.3/49.7	75.9, 119.3	19, 17
24.9/75.1	93.1, 125.8	12, 14
12.4/87.6	85.4, 117.2	14, 17
(2) aPMMA/PVP1		
100/0	102.7	12
87.5/12.5	105.7	9
75.3/24.7	106.2	9
50.1/49.9	106.6	7
24.7/75.3	105.8	11
12.5/87.5	118.3	16
(3) sPMMA/PVP1		
100/0	122.4	13
87.1/12.9	128.5	13
75.3/24.7	127.8	13
49.9/50.1	128.8	13
25.5/75.5	126.8	14
0/100	128.7	22
74.9/25.1	128.9	
49.8/50.2	129.2	
25.0/75.0	126.7	
0/100	118.3	

Table III Glass transition temperatures of chloroform-cast PMMA/PVP2 blends

	T_g (℃)	ΔTg (℃)
(1) iPMMA/PVP2		
100/0	74.6	20
75.1/24.9	77.0, 116.1	17, 15
49.8/50.2	81.7, 120.3	15, 15
24.9/75.1	91.7, 125.2	15, 8
(2) aPMMA/PVP2		
100/0	102.7	12
74.6/25.4	106.2	6
50.4/49.6	104.7	11
24.9/75.1	108.1	17
(3) sPMMA/PVP2		
100/0	122.4	13