Supplementary Information for:

Chain entanglement and molecular dynamics of solution-cast PMMA/SMA blend films affected by hydrogen bonding between casting solvents and polymer chains

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Determination of Concentration regime of PMMA/SMA (20/80) solutions

It is well known that the concentration of polymer solution can be divided into three main regimes: dilute, semi-dilute and concentrated solution by c*(critical overlap concentration) and c_e (entanglement concentration), respectively. For certain polymer, c^* can be obtained by theoretical calculation or rheological experiment. The definition of c* derived from polymer physics is suggested

$$c^* = \frac{3M_w}{4\pi N_A {R_g}^3} = 3M_W/4\pi N_A a^3 N^{1.8} \tag{1}$$

Where M_w is the molecular weight, N_A is Avogadro's number, R_g is the radius of gyration, a is the length of Kuhn, N is the degree of polymerization.

For blends, c* can be calculated using

$$c^* = 3(M_{w1}x_1 + M_{w2}x_2)/4\pi N_A a^3 (N_1 x_1 + N_2 x_2)^{1.8} \tag{2}$$

where the x is the weight fraction, and the subscripts 1 and 2 refer to components 1 and 2, respectively. In this study, the calculated c* of PMMA/SMA (20/80) blend solution by using eq.(2) is about 3.25g/L. Considering the density of m-xylene and acetic acid used being 0.86 and 1.05g/cm^{-3} respectively, c* of the mixed solutions with R_{ac} from 0 to 0.4 ranges from 3.5 to 3.8$\times$10^{-3} in weight fraction. In addition, the entanglement concentration c_e can be estimated to be about 10c*, according to the method by R. H. Colby [*Rheol Acta* **2010**, 49, 425-442]. Hence, the 5% wt solutions investigated in this work are in the concentrated regime.

In the solutions of concentrated regime investigated in the paper, polymer coils are overlapped so the performances of solution-cast blend films will mainly affected by the entanglement density.

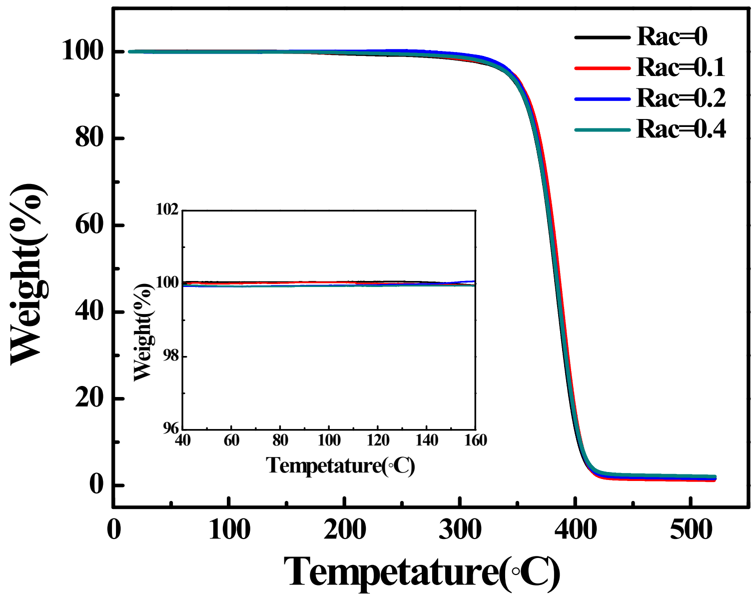

Fig. S1 TGA plots of PMMA/SMA (20/80) blend films cast from component solvents composed of m-xylene and acetic acid with different mass ratio of acetic acid (R_{ac}). The inlay presents the partial enlargement of the plots.

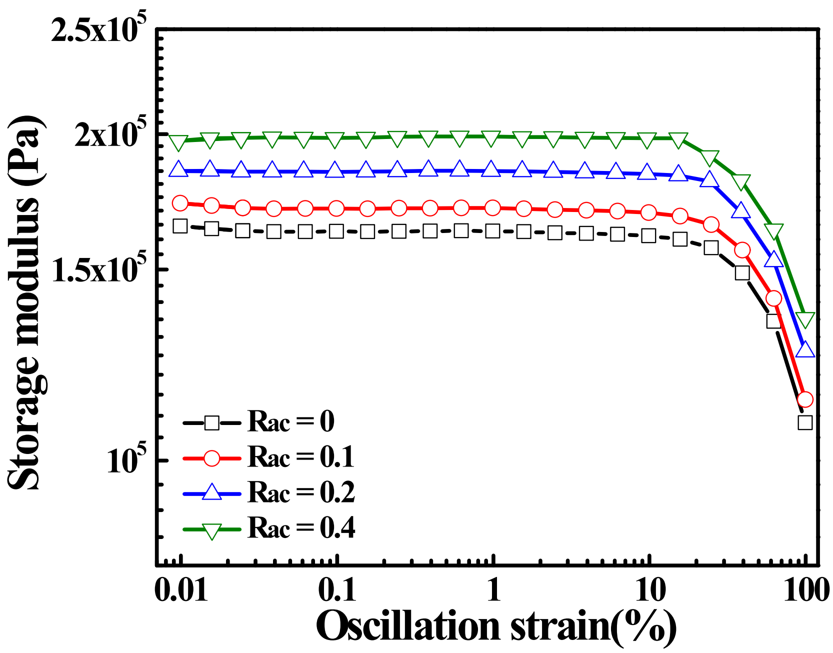

Fig. S2 Strain dependences of storage modulus of various PMMA/SMA (20/80) solution-cast samples at the the temperature of 160°C and at the angular frequency of 1 rad/s. (R_{ac}=0, 0.2, 0.4, R_{ac} refers to the mass ratio of acetic acid in acetic acid/m-xylene mixed solvents).

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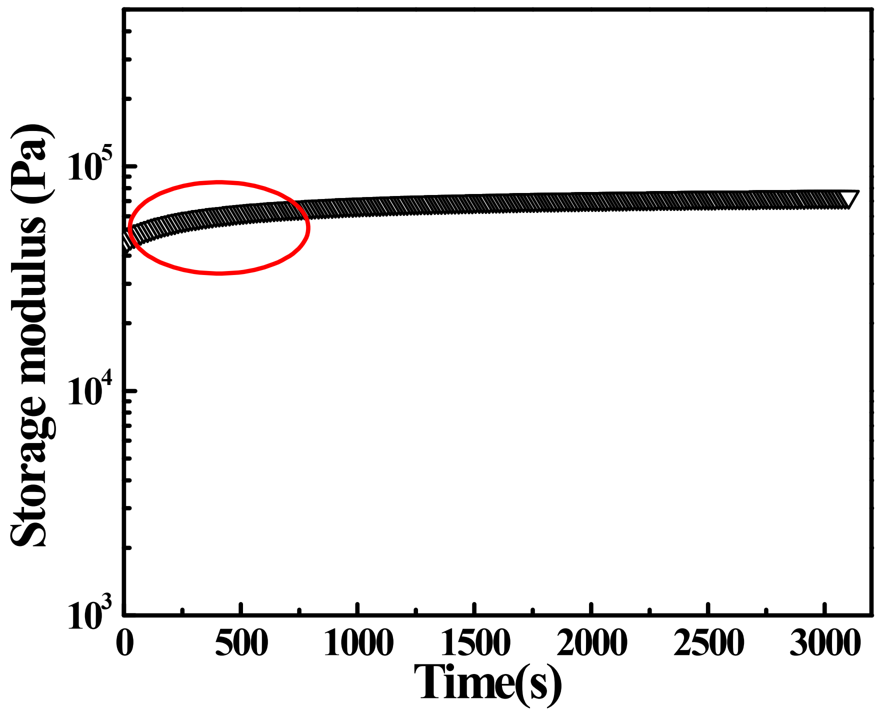

Fig. S3 Time dependences of storage modulus of melt blending PMMA/SMA(20/80) sample with a 1% strain at the angular frequency of 1 rad/s and the temperature of 160°C.

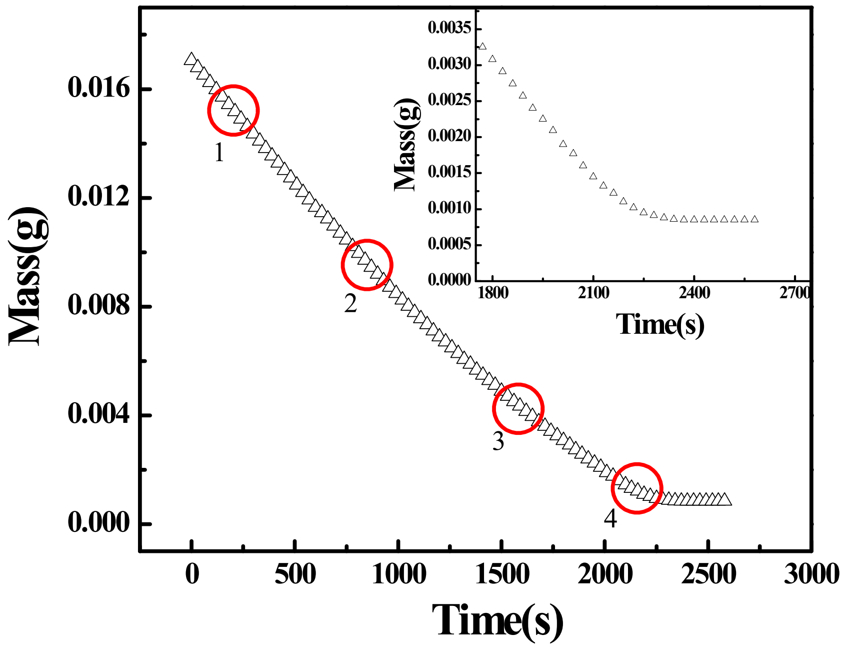

Fig. S4 Volatilization curve of PMMA/acetic acid solution with a weight concentration of 5% at 25 ^{o}C.

The volatilization process of the 5 wt% PMMA/acetic acid solution at 25 ^{o}C was presented in Fig. S3 by recording the residual mass of a drop of solution and the corresponding time in an electric balance with a precision of $\pm 10^{-5}$ g. It can be seen that the evaporation rate of the acetic acid decreases gradually as the time passed. When the time comes to the 32nd min, the mass achieved to a balance, indicating that the acetic acid has been removed totally. The FTIR spectra of the acetic acid solution of PMMA were recorded in different stages shown in Fig. S3.

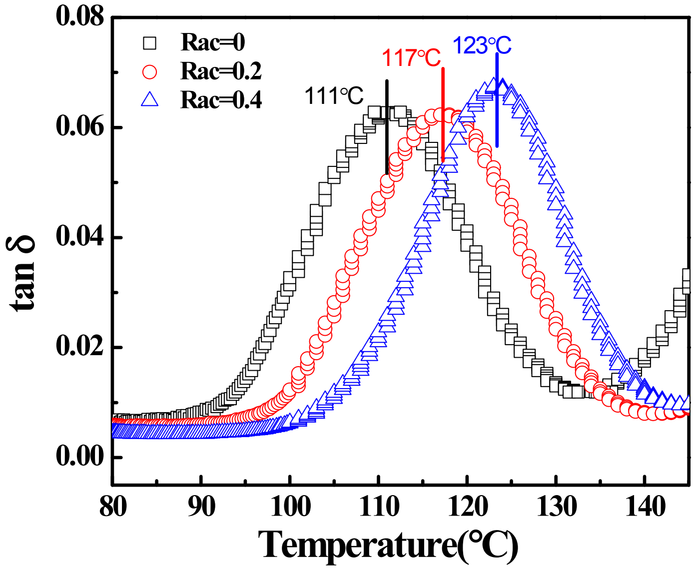

Fig. S5 Temperature dependence of tan δ for PMMA/SMA(40/60) blend films cast from different solvents(R_{ac}=0, 0.2, 0.4, R_{ac} refers to the mass ratio of acetic acid in acetic acid/m-xylene mixed solvents).

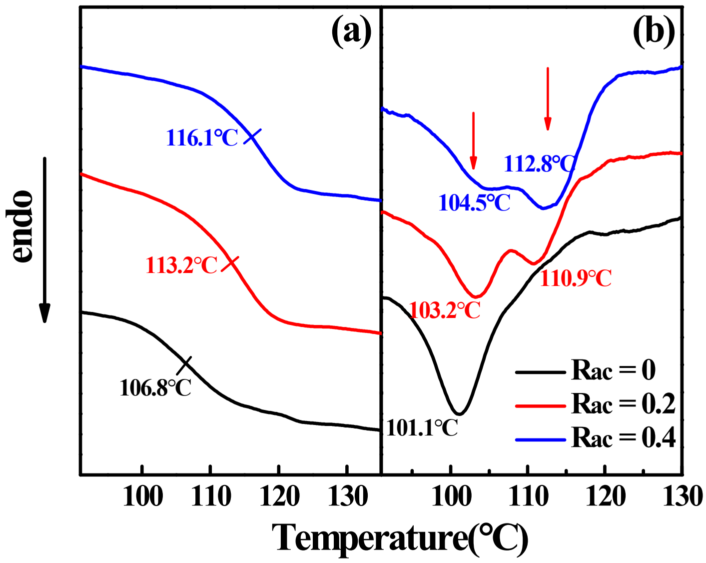

Fig. S6 Variation of reversing (a) and non-reversing (b) heat flow with temperature for PMMA/SMA (40/60) blend films cast from solvents with different R_{ac}. The DSC results were obtained in the modulated mode while heating with temperature modulation amplitude of 0.5^{o}C and an oscillation period of 60s.