

TRANSESTERIFICATION IN POLYPHENYLSILSISQUIOXANE (PPSQ)/POLY ETHYLENE TERE- PHTHALATE (PET) BLENDS*

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ABSTRACT

The chemical structure of copolymer formed in the transesterification of PPSQ/PET blends during melt-processing is deduced from the ^1H -NMR spectra. The transesterification extent of this blend is interpreted by the changes of crystalline melting peak in DSC thermograms of the insoluble products containing unreacted PET and some block PPSQ segments. Effects of composition of blend ladderlike regularity of PPSQ on the reaction extent have also been discussed. Inclusion of some block PPSQ segments in PET has no influence on the crystalline morphology of PET.

INTRODUCTION

Recently, there has been considerable scientific and industrial interest in the transesterification of polyesters. Transesterification in PC/PET and PBT/Polyarylate blends had been studied by many researchers^[1-4].

Polyphenylsilsisquioxane (PPSQ), one kind of ladderlike polymers, has

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many good properties, such as thermal and oxidative stability, excellent solubility in many common solvents, electric insulating property and selective permeability to gases. Since 1984, Shi and his coworkers in our laboratory had studied the synthesis, solution property, structural characterization, thermal and degradation of PPSQ^[5-10]. Films of PPSQ could not be applied widely because of their poor strength. It is well known that film of PET is strong and easy to be prepared. But, PPSQ and PET are incompatible in view of the difference in their solubility parameters. The compatibility of the two polymers could be improved if unreacted hydroxyl (-OH) groups in the backbone of PPSQ were reacted with the ester groups in PET. In this study, chemical structure of copolymers formed in transesterification of PPSQ/PET blends is deduced from ¹H-NMR spectra. The effect of reaction conditions on the extent of transesterification has also been discussed.

EXPERIMENTAL

Preparation of samples

Three samples of PPSQ have been synthesized by ourselves. The weight-average molecular weights of PPSQ(L), PPSQ(M) and PPSQ(H) determined by GPC are 2.19×10^3 , 0.92×10^4 and 5.42×10^4 , respectively. Their percentage of defective Si-atoms attached to OH which was calculated from their ²⁹Si-NMR spectra^[5] are 50%, 23.6% and 0. PET was a commercial product. All blends with different compositions (shown in Table 2) were prepared in weight percentage. PPSQ and PET in designed proportions were first dissolved in the mixed solvents (phenol : 1,1,2,2-tetrachloroethane in a 60 : 40 ratio by volume). After dissolving completely, the blend was precipitated with methanol and then was dried in a vacuum oven at 60°C for one day and kept in a desiccator at room temperature for a few weeks.

Transesterification of PPSQ/PET blends was carried out in a heated tube without stirring which was put into a silicone oil bath under dry nitrogen. The blends with different reaction extent were obtained by changing the reaction conditions.

The final products after transesterification were extracted in benzene for several days. The insoluble products after extraction including unreacted PET

and some PET-b-PPSQ were dried for ^1H -NMR and DSC analysis.

Measurements

^1H -NMR spectra of PPSQ, PET and their insoluble blend products were recorded on JHX-FX100 nuclear magnetic instruments (JBOX) operating at 100 MHz. NMR samples were prepared by dissolving the insoluble blend products in a 50/50 mixture of deuterated chloroform and deuterated trifluoroacetic acid. PET and PPSQ were dissolved in deuterated trifluoroacetic acid and deuterated chloroform, respectively. Tetramethylsilane was used as an internal standard.

Measurement of melting points and heat of fusion of selected samples was accomplished with a Perkin Elmer differential scanning calorimeter (DSC-4). The range of temperature was from room temperature to 280 °C. A heating rate of 20 °C/min was used in all cases and the melting heat per gram were calculated by computer.

The crystalline morphology of PET in some insoluble blend products was investigated by OLYMPUS BH-2 polarization microscopy. Samples for this measurement were prepared as follows. Insoluble products or PET were heated to 280 °C. When they were completely melted, then pressed into thin films. These films were cooled to 180 °C and kept at this temperature for half an hour. Finally, these samples were cooled spontaneously to room temperature.

RESULTS AND DISCUSSION

The ^1H -NMR spectra of PPSQ(L), PPSQ(M) and PET are shown in Fig. 1a and 1b with peak assignments. The ^1H -NMR spectra of the extracted insoluble products including unreacted PET and PET blocked into some PPSQ segments for PPSQ(M)/PET (50/50) and PPSQ(L)/PET (50/50) blends which were heat-treated at 280 °C for 5 min during the transesterification are indicated in Fig. 2a and 2b, respectively. The possible peak assignments and intensity of some peaks are also given in Table 1. As would be expected, there are not only typical chemical shifts of PET but also chemical shifts of PPSQ segments coexisted in the ^1H -NMR spectra (Fig. 2). From Table 1, the intensity of peak at 4.85 ppm is higher than that of peak at 8.19 ppm in these blends because the peak at 4.85 ppm attributed to PET is superimposed with the one at 4.8 ppm caused by -OH of PPSQ.

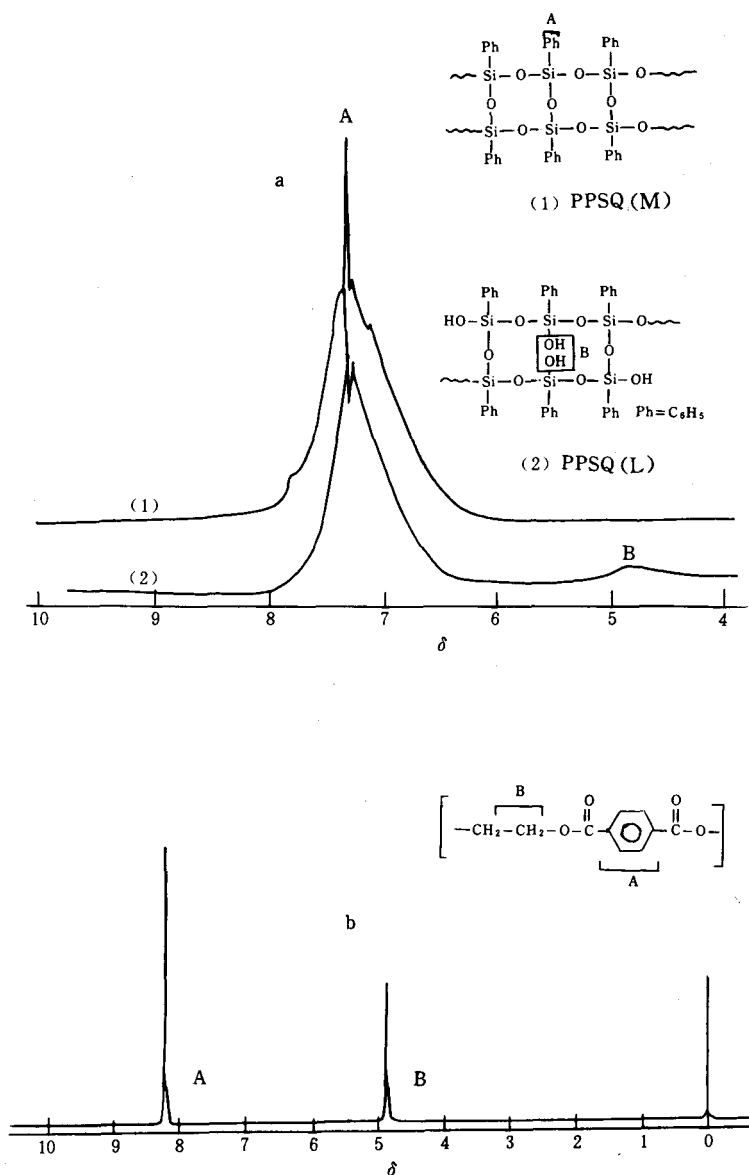


Fig. 1 $^1\text{H-NMR}$ spectra of (a) PPSQ(M) and PPSQ(L) and (b) PET

In addition, one new peak corresponding to 4.2 ppm appears in both Figs. 2 (a) and 2(b). According to the literature,^[11] peak at about of 4.1 ppm in NMR spectrum of ethylene glycol is attributed to $-\text{OH}$. Peak at 4.2 ppm in NMR spectra of the insoluble blend products can be explained as the formation of some PET- $\text{CH}_2\text{CH}_2\text{OH}$ in the transesterification of these blends. Typical peaks of $^1\text{H-NMR}$ spectra for the insoluble products do not shift by comparing with

the peaks of pure PET and PPSQ. This result means that the copolymer in this blend did not affect the chemical shifts of PET and PPSQ. From the above discussion, the chemical structure of the copolymer can be deduced as PET-COO-Si-PPSQ. The possible scheme of transesterification reaction in PPSQ/PET blends during melt-processing may be proposed as follows.

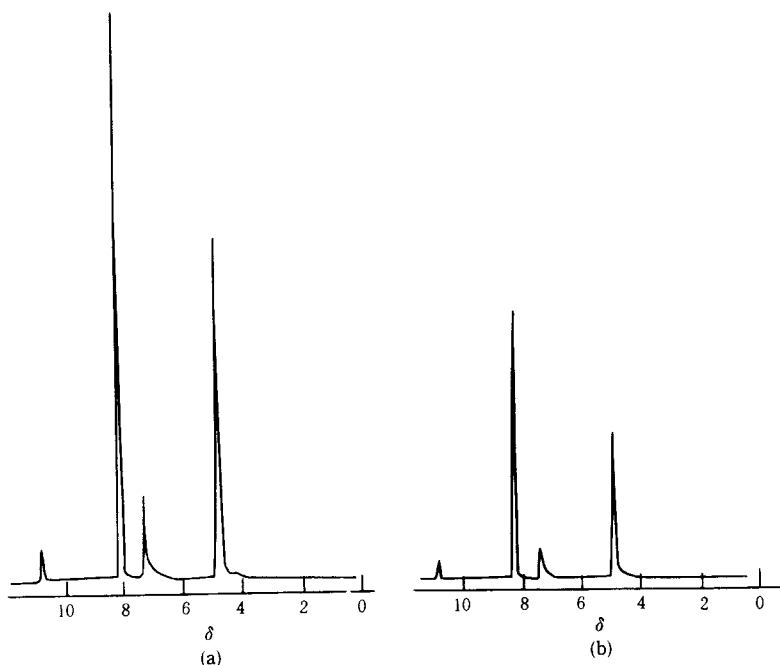
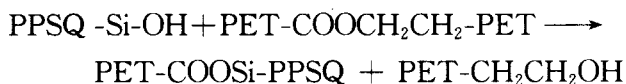


Fig. 2 $^1\text{H-NMR}$ spectra of (a) M5 and (b) L5 which are the extracted insoluble products of PPSQ(M)/PET (50/50) and PPSQ(L)/PET (50/50)

Transesterification conditions of PET/PPSQ blends and the DSC data of all samples are shown in Table 2. Maximum temperatures ($T_{\max}$) of the melting peaks of all blends are slightly lower than that of PET. From T_i (initial point of melting) and T_f (final point of melting), it is clear that the melting peaks of these blends are broader than that of pure PET. The melting heat per gram of H5 is higher than that of H5[#] because H5[#] was not extracted, hence contained much more PPSQ molecules. This result indicates that the inclusion of PPSQ

Table 1 Positions(δ) and intensity (I) of some typical peaks in ^1H -NMR spectra of PET and its blends with PPSQ

Names of samples	δ (ppm)	I (%)	δ (ppm)	I (%)	δ (ppm)	I (%)	δ (ppm)	I (%)
PET	8.19	49.6	4.85	49.6				
M5 ^{a)}	8.19	39.5	4.85	40.5	7.35	16.1	4.20	1.9
L5 ^{a)}	8.19	40.6	4.85	44.2	7.35	10.3	4.20	2.2

a) Samples M5 and L5 are the extracted insoluble products of PPSQ(M)/PET (50/50) and PPSQ(L)/PET (50/50) which were heated at 280°C for 5 min.

segments in PET can reduce the crystallinity of PET and the melting heat per gram of the blends. Therefore, the transesterification extent of these blends can be reflected by the change of the melting heat per gram for the insoluble products. The reaction extent increases with a decrease of the melting heat. Due to inclusion of more PPSQ molecules in the unextracted blend sample, the melting heat of extracted sample M2 is higher than that of unextracted sample M2[#]. It is easily noticed that the melting heat of sample M5 is the smallest among samples M8, M5 and M2. So, the transesterification extent of sample M5 with a composition 50/50 is the highest among the three samples prepared under the same reaction conditions except their compositions. The melting heat of sample M5 after a short reaction time (5 min) is less than that of M5* after a long reaction time (20 min). This conclusion can also be obtained from samples L5 and L5*. The possible reason is that some molecules of PET-b-PPSQ, in which PET chains were short due to the deeper degradation of PET resulting from longer reaction time, were dissolved in the solvent when the final reaction products were extracted by benzene. That the melting heat per gram of samples L5, M5 and H5 increase with the ladderlike regularity of their structure demonstrates the influence of PPSQ's structure on the transesterification in these blends. The degree of reaction of sample L5 is the greatest because PPSQ(L) has the most Si-OH groups. On the other hand, there is almost no transesterification in PPSQ(H)/PET (50/50) blend because of the perfect ladderlike structure of PPSQ(H). So, the appropriate transesterification conditions in which the reaction degree is the highest should be as follows: the composition of blend (50/50) and PPSQ with much more Si-OH groups.

Table 2 Transesterification condition of PET/PPSQ and their DSC data

No. ^{a)}	PPSQ/PET	Transesterification condition	Crystalline melting peak of PET			
			$T_i(^{\circ}\text{C})$	$T_f(^{\circ}\text{C})$	$T_{\text{max}}(^{\circ}\text{C})$	Cal/Gram
M8	80/20	280 $^{\circ}\text{C}$ /5min	176.0	265.0	254.0	11.63
M5	50/50	280 $^{\circ}\text{C}$ /5min	189.7	263.5	253.0	9.19
M5*	50/50	280 $^{\circ}\text{C}$ /20min	217.1	263.2	255.6	11.11
2 [#]	20/80 ^{b)}	280 $^{\circ}\text{C}$ /5min	186.5	269.0	250.4	10.68
H5	50/50	280 $^{\circ}\text{C}$ /5min	219.1	264.4	251.2	12.08
H5 [#]	50/50 ^{b)}	280 $^{\circ}\text{C}$ /5min	165.1	269.7	252.1	9.33
L5	50/50	280 $^{\circ}\text{C}$ /5min	219.8	263.5	253.6	7.02
L5*	50/50	280 $^{\circ}\text{C}$ /20min	221.2	265.6	254.2	11.44
0	0/100	280 $^{\circ}\text{C}$ /5min	219.8	264.9	255.9	11.18

a) The ladderlike structure of PPSQ(H) in samples H5 and H5[#] is the most perfect and the structure of PPSQ(M) in samples M8, M5, M5* and M2[#] is the second most perfect. PPSQ(L) in samples L5 and L5* has the most defects in its structure

b) Samples M2[#] and H5[#] were not extracted

Polarization micrographs of four samples prepared under the same crystallization conditions are shown in Fig. 3. There are many overlapped little spherical crystallites in the micrograph of pure PET (Fig. 3(a)). The only difference between Fig. 3(a) and 3(b) is that some black domain (amorphous phase) in Fig. 3(b) formed by the PPSQ segments blocked with PET are dispersed in the continuous PET crystalline phase. Sample L5 (Fig. 3(c)) has much bigger domain of the PPSQ amorphous phase than sample M5 (Fig. 3(b)) and some black domains are interconnected. This phenomenon also demonstrates that there are much more blocked PPSQ segments in sample L5 than in M5. No difference between micrograph of sample M5* (Fig. 3(d)) and that of PET indicates that the sample M5* contains a small amount of PET-b-PPSQ molecules. These conclusions are the same as that deduced from the analysis of DSC data. From all the polarization micrographs of four samples, crystalline morphology of these insoluble products are similar to that of pure PET. Therefore, inclusion of some blocked PPSQ segments in PET has no effect on the crystalline morphology of PET although this inclusion can reduce the crystallinity of PET.

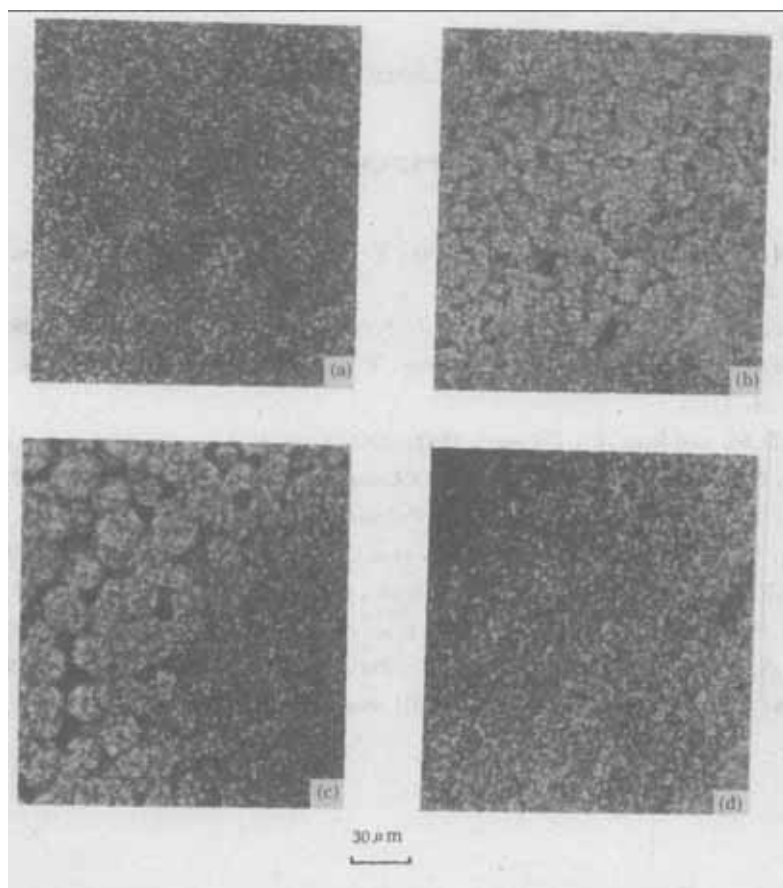


Fig. 3 Polarization micrographs of (a) PET, (b) M5, (c) L5 and (d) M5*
(The numbers of samples correspond to those in Table 2)

CONCLUSIONS

Chemical structure of copolymer formed in PPSQ/PET transesterification has been deduced from ^1H -NMR spectra of two insoluble products. The possible transesterification reaction scheme in these blends is also proposed. DSC data show that the extents of transesterification in PPSQ/PET blends were determined by the composition of blends and the ladderlike regularity of PPSQ. Sample L5 has the highest transesterification extent because its composition is 50/50 and PPSQ(L) has the most Si-OH groups. Some conclusions from DSC data are in conformity with those from polarization micrographs. In addition, the

micrographs of some selected samples indicate that the inclusion of some block PPSQ segments in PET has no effect on the crystalline morphology of PET.

Keywords:

Transesterification; Polyphenylsilsisquioxane/PET blend

REFERENCES

- [1] Godard, P. ; Dekoninck, J. M. ; Pevlesaver, V. , et al. , *J. Polym. Sci. , Polym. Chem. Ed. ,* **1986**, 24, 3301.
- [2] Devaux, J. ; Godard, P. , Mercier, J. P. , *J. Polym. Sci. , Polym. Phys. Ed. ,* **1982**, 20, 1875.
- [3] Godard, P. ; Dekoninck, J. M. ; Pevlesaver, V. , et al. , *J. Polym. Sci. , Polym. Chem. Ed. ,* **1986**, 24, 3315.
- [4] Miley, D. M. and Runt, J. , *Polymer*, **1992**, 33(21), 4643.
- [5] Zhang, X. S. ; Chen, S. M. ; Shi, L. H. , *Chinese J. Polym. Sci. ,* **1987**, 5(2), 162.
- [6] Zhang, X. S. and Shi, L. H. , *Chinese J. Polym. Sci. ,* **1987**, 5(3), 197.
- [7] Huang, C. R. ; Xu, G. Z. ; Zhang, X. S. , et al. , *Chinese J. Polym. Sci. ,* **1987**, 5(4), 347.
- [8] Zhang, X. S. ; Shi, L. H. ; Huang C. R. , et al. , *Chinese J. Polym. Sci. ,* **1987**, 5(4), 352.
- [9] Shi, L. H. ; Zhang, X. S. ; Huang C. R. , et al. , *Chinese J. Polym. Sci. ,* **1987**, 5(4), 359.
- [10] Zhang, X. S. ; Shi, L. H. ; Li, S. Q. , et al. , *Polymer Degradation and Stability*, **1988**, 20, 157.
- [11] Charles, J. P. , *The Aldrich Library of NMR Spectra*, Aldrich Chemical Company Inc. , **1983**, p. 120.