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*FT*i.r. study of graft copolymer compatibilizers for blends of functionalized polypropylene and liquid-crystalline polyester

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Graft copolymers of polypropylene functionalized with 6 wt% of acrylic acid (PPAA) and a liquid-crystalline polyester (SBH) derived from sebacic acid, 4,4′-dihydroxybiphenyl and 4-hydroxybenzoic acid, prepared under various conditions, as well as fractionation products of the graft copolymers were investigated by infra-red spectroscopy. The grafting was followed by measuring changes in the amount of carboxylic and aliphatic–aromatic ester groups. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: functionalized polypropylene; liquid-crystalline polyester; graft copolymers)

INTRODUCTION

Blends of thermoplastics and liquid-crystalline polymers (LCPs) have attracted considerable attention recently as new materials with improved properties. However, because the majority of thermoplastics are not compatible with liquid-crystalline polymers, it is necessary to use compatibilizers in order to improve miscibility of the blend components. The compatibilizers are usually block or graft copolymers having a structure identical to that of the blend components.

The aim of our investigations was to determine the structure of compatibilizers comprising graft copolymers of polypropylene functionalized with 6 wt% of acrylic acid (PPAA, Polybond 1001) and the constituents of SBH liquid crystalline polymer, i.e. sebacic acid, biphenyldiol and hydroxybenzoic acid. The fractionation products of the copolymers [fractions soluble in toluene (STCP) and in xylene (SXCP), and insoluble residue (RXCP)], the mixtures of PPAA with SBH polymer (MIXP) and their fractionation products (STMP, SXMP, RXMP) were also investigated. An attempt was made to determine the structure of the polymers under study by means of Fourier transform infra-red spectroscopy (*FT*i.r.).

EXPERIMENTAL

Materials

In this work the following three groups of the products were characterized:

- mixtures (MIXP) of PPAA with liquid-crystalline polyester SBH (PPAA contents of 50% and 70%, designated as MIXP50 and MIXP70, respectively);
- copolymers (COPP) of PPAA with the monomers from which polyester SBH was made (PPAA contents of 50% and 70%, designated COPP50 and COPP70, respectively); and
- the products of extractions of COPP50 and MIXP50.The extraction procedures and the sample designations are presented in *Scheme 1*.

Measurements

Infra-red spectra were recorded on a BIO-RAD FTS 40A spectrometer. The specimens were in the form of KBr pellets. A curve-fitting program was used in order to determine quantitative relationships among the five kinds of carbonyl group (aliphatic–aromatic ester, aromatic–aromatic ester, free acid, associated acid and associated ester) which give rise to the overlapped bands in the 1850–1660 cm^{-1} range corresponding to C=O stretching vibrations. The initial parameters were obtained from the second derivative spectra. The interactive procedure and Gauss–Lorentz type of curves were chosen to correct these parameters and to compute particular peaks.

For quantitative determination of the ratio of the amount of PPAA to SBH component in the reaction products and fractionated samples, the second derivative spectra were used. The second derivatives were calculated with the aid of a WIN IR arithmetic program, by using the Savitsky–Golay method (degree of polynomial = 2, number of convolution points = 20) and the baseline-to-peak technique.

RESULTS AND DISCUSSION

In our previous studies[1–3] the graft copolymers of functionalized polyethylene (PEox) and the liquid-crystalline polyester SBH were investigated by means of *FT*i.r. The same method and procedure[3] were used in the present work, which focused on the characterization of graft copolymers of functionalized polypropylene (PPAA) and SBH.

Analysing the spectrum of PPAA (*Figure 1*) and the data obtained from the curve-fitting calculations (*Table 1*, no. 2) we have found two bands, at 1740 cm^{-1} (weaker) and at 1711 cm^{-1} (stronger), arising from free and associated acid C=O groups, respectively. The bands corresponding to

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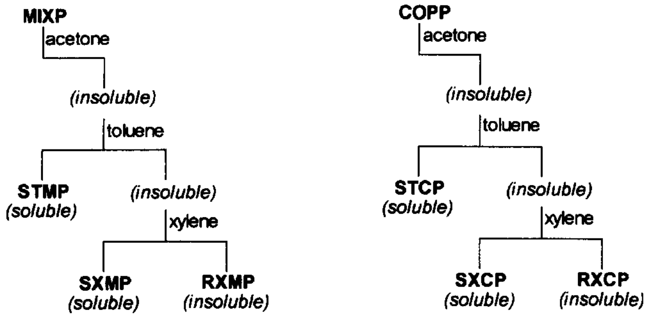

Scheme 1

CH_2 and CH_3 groups are observed in the 2900–2800 cm^{-1} region and at 1460, 1377, 1358, 997, 973 and 842 cm^{-1}. The bands with rather small intensity in the 1300–1100 cm^{-1} region are due to the vibrations of C–O– acid groups.

In the spectrum of SBH, the band at 1731 cm^{-1} corresponding to C=O aromatic–aromatic ester groups was found to be overlapped with the band at 1758 cm^{-1} arising from aliphatic–aromatic ester groups. Very weak bands appearing at 1740 cm^{-1} and 1714 cm^{-1} were attributed to the vibrations of free and associated acid groups, respectively (*Table 1*, no. 1). This proves that a small amount of acid groups is present in SBH. The bands characteristic for aromatic ring vibrations appear at 1600,

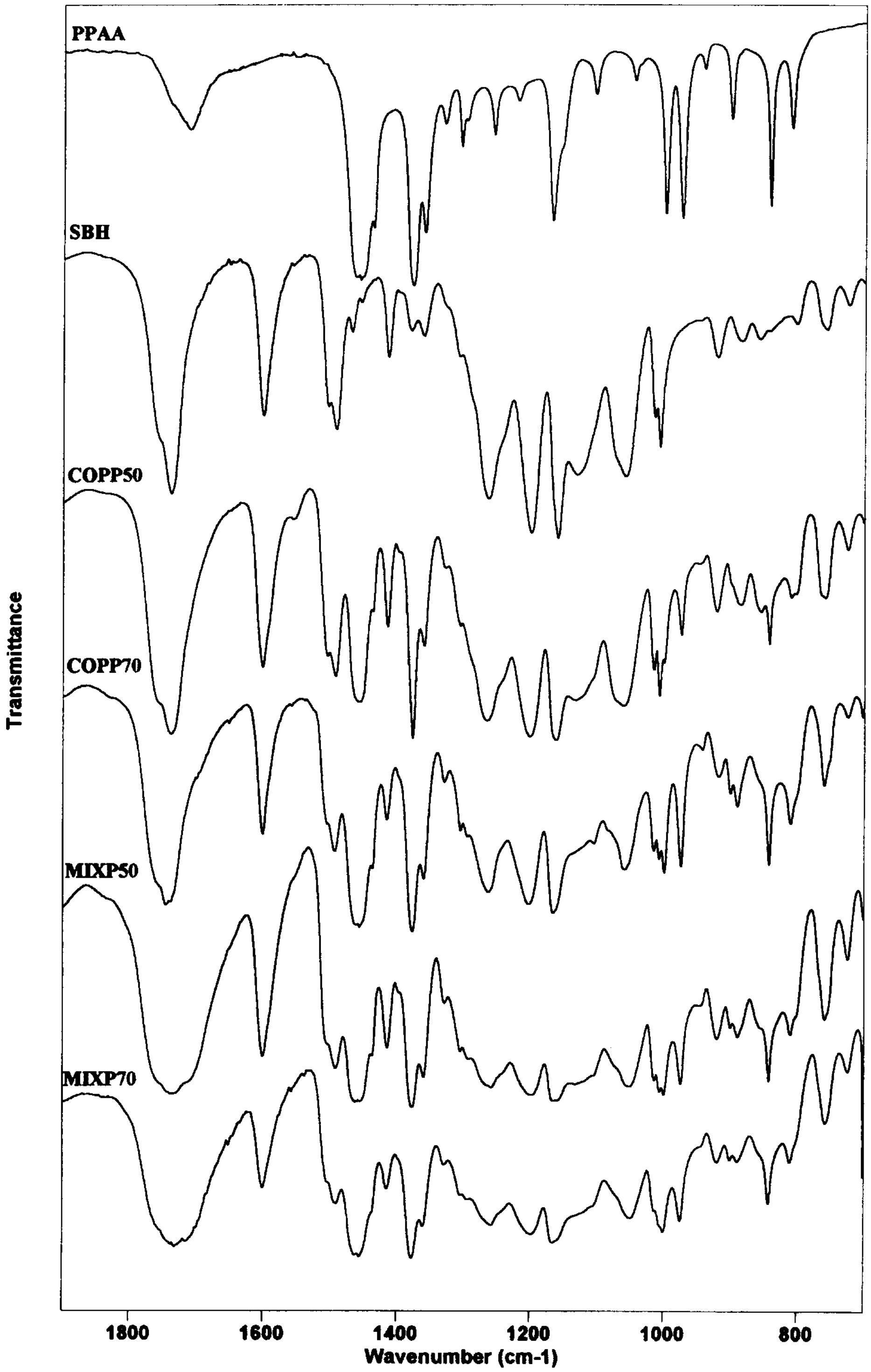

Figure 1 *FT*i.r. spectra of mixing and copolymerization reaction products

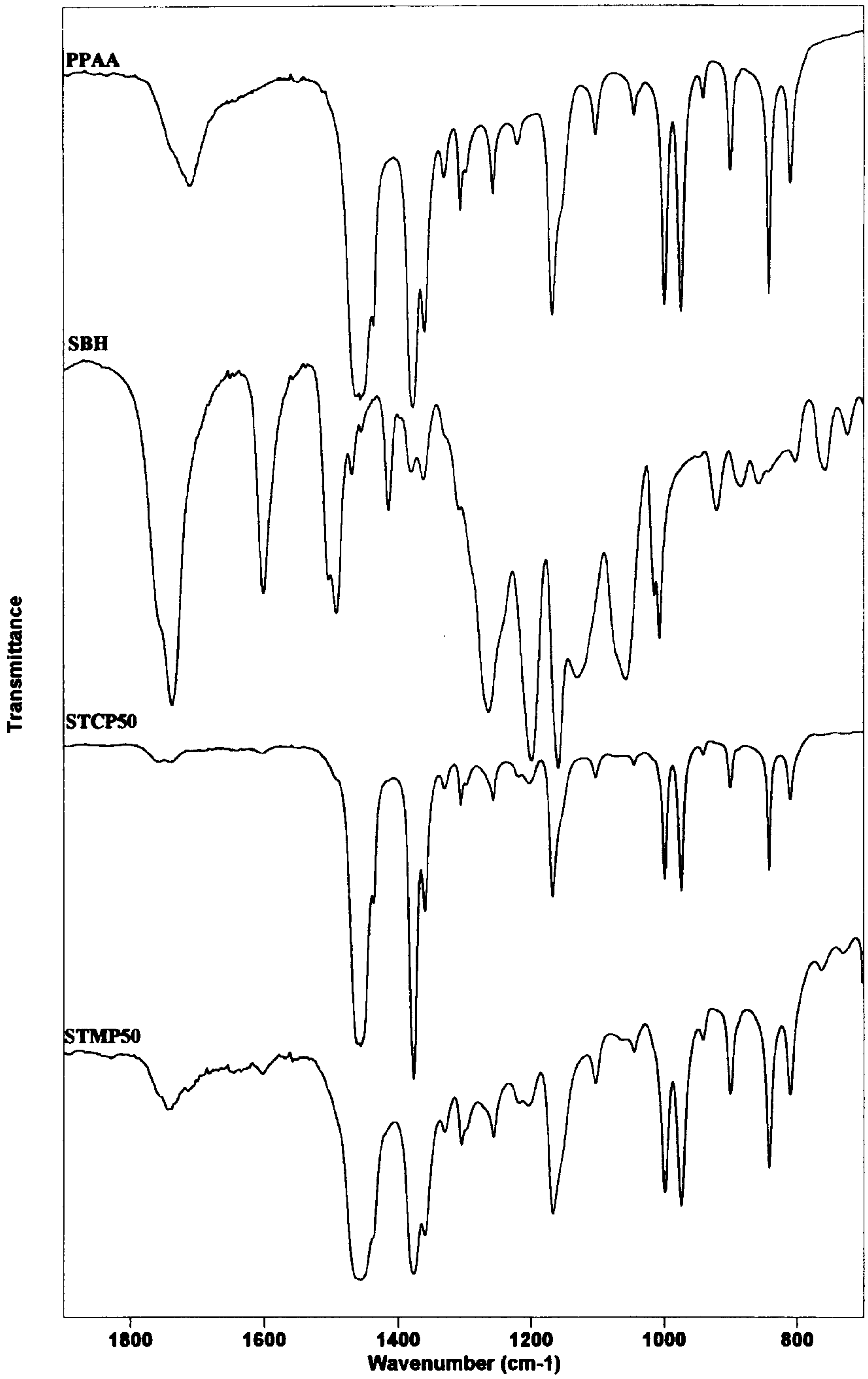

Figure 2 *FT*i.r. spectra of the fractions soluble in toluene

1500 and 1006 cm^{-1}. The bands arising from aliphatic $-CH_2-$ groups were also present, although shifted slightly and with lower intensity compared with those observed in PPAA.

As seen in *Figure 1*, the bands characteristic for both components (PPAA and SBH) can also be observed in the spectra of the copolymers (COPP) and mixtures (MIXP). The main differences concern the bands corresponding to C=O ester and acid groups. In the case of COPP50 and COPP70 the shape of this band is similar to that of SBH. Comparing the results of curve-fitting calculations obtained for the copolymers, it can be noticed that more unreacted free C=O acid groups appear in the case of COPP70 than in COPP50 (*Table 1*, nos. 3 and 4), which is due to the higher content of PPAA (and acid groups) in COPP70.

For MIXP50 and MIXP70 the bands arising from C=O ester and acid groups are broader than in the case of COPP50 and COPP70. Curve-fitting calculations reveal the presence of an additional band at about 1690 cm^{-1}, which can be assigned to the vibrations of associated C=O ester groups. This observation may indicate that, in the samples being mixtures, hydrogen bonds were formed between the C=O ester groups from SBH and OH acid groups from

Table 1 'Curve-fitting' calculations of the areas of C=O groups of aliphatic–aromatic ester ($A_{\mathrm{al-ar}}$), aromatic–aromatic ester ($A_{\mathrm{ar-ar}}$), free acid (A_{afree}), associated acid (A_{aass}) peaks and associated ester (A_{eass})

		C=O aliphatic–aromatic ester band		C=O aromatic–aromatic ester band		C=O free acid band		C=O associated acid band		C=O associated ester band	
No.	Sample[a]	ν (cm^{-1})	$A_{\mathrm{al-ar}}/A_{\mathrm{T}}$ [b]	ν (cm^{-1})	$A_{\mathrm{ar-ar}}/A_{\mathrm{T}}$ [b]	ν (cm^{-1})	$A_{\mathrm{afree}}/A_{\mathrm{T}}$ [b]	ν (cm^{-1})	$A_{\mathrm{aass}}/A_{\mathrm{T}}$ [b]	ν (cm^{-1})	$A_{\mathrm{eass}}/A_{\mathrm{T}}$ [b]
1	SBH	1758	0.510	1731	0.262	1740	0.197	1714	0.030		
2	PPAA					1740	0.233	1711	0.766		
3	COPP50	1759	0.452	1729	0.121	1741	0.134	1716	0.291	1694	0.002
4	COPP70	1761	0.409	1734	0.116	1746	0.164	1722	0.298	1693	0.010
5	MIXP50	1764	0.262	1730	0.206	1744	0.092	1710	0.241	1690	0.198
6	MIXP70	1764	0.218	1730	0.143	1744	0.253	1709	0.142	1689	0.244
7	RXCP50	1762	0.407	1730	0.185	1741	0.313	1713	0.090	1692	0.004
8	RXMP50	1762	0.515	1730	0.106	1741	0.269	1720	0.091	1697	0.019
9	SXCP50	1758	0.478	1732	0.175	1740	0.155	1723	0.190		
10	SXMP50	1761	0.233			1743	0.149	1711	0.619	1695	0.020
11	STMP50[c]	1757		1737				1714			
12	STCP50[c]	1761		1737				1720		1699	

[a] Sample designations as in *Scheme 1*

[b] $A_{\mathrm{T}} = A_{\mathrm{al-ar}} + A_{\mathrm{ar-ar}} + A_{\mathrm{afree}} + A_{\mathrm{aass}} + A_{\mathrm{eass}}$

[c] Owing to the low absolute value of the total area, the results of the curve-fitting calculations can be erroneous

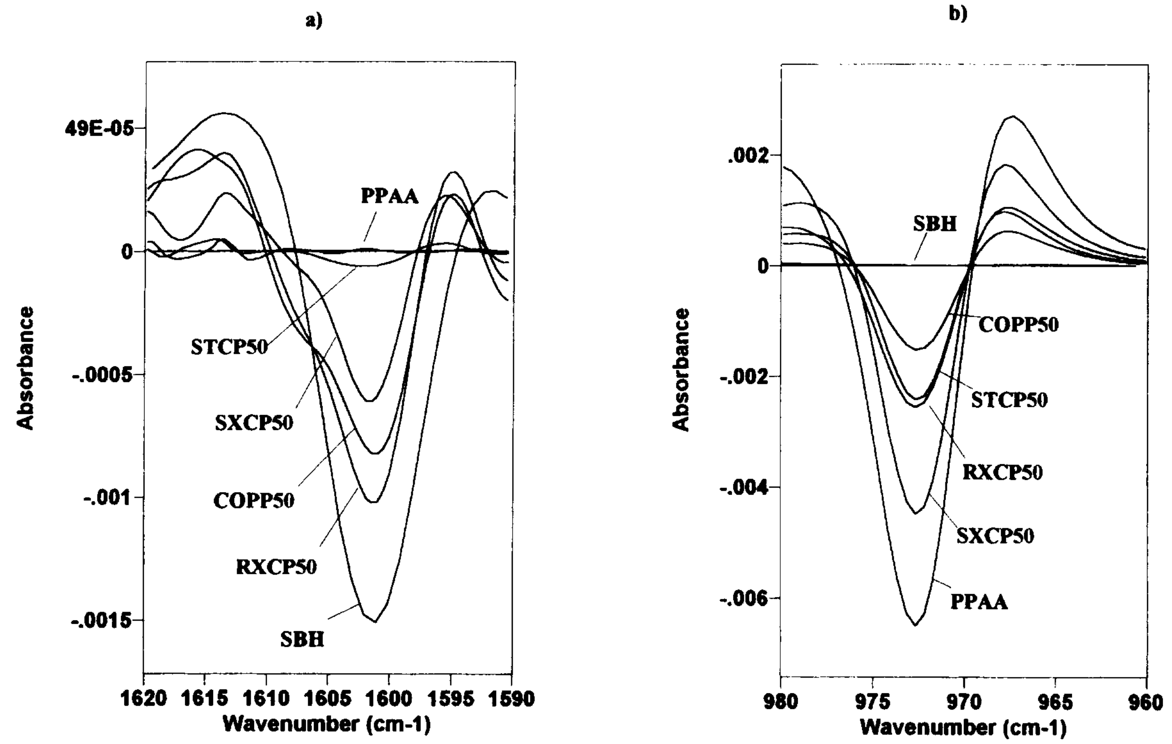

Figure 3 The second derivative spectra of COPP50 and its fractionation products

Table 2 The ratio of the second derivatives at 973 cm^{-1} and 1600 cm^{-1}

Sample[a]	${}^{2}D_{973}/{}^{2}D_{1600}$
COPP50	1.85
COPP70	2.10
MIXP50	2.24
MIXP70	2.32
RXCP50	2.51
RXMP50	0.09
SXCP50	5.82
SXMP50	6.48
STMP50	23.33
STCP50	20.00

[a] Sample designations as in *Scheme 1*

PPAA. In the case of MIXP70 the area of the band at 1690 cm^{-1} is larger than that for MIXP50. On the other hand, in MIXP70, the area of the band ascribed to free C=O acid groups is larger whereas that of associated acid groups is smaller than the respective bands of MIXP50. This means that in MIXP70 more ester groups participate in the formation of hydrogen bonds, evidently because of a higher content of PPAA (and acid groups) in this sample. Curve-fitting calculations indicate also that more aliphatic–aromatic ester bands and fewer acid bands appear in the case of the copolymers (*Table 1*, nos. 3 to 6) than in the corresponding mixtures. This may indicate that carboxylic groups from PPAA react during polycondensation.

Also, some differences can be seen in the spectra of the extraction products. The spectra obtained for

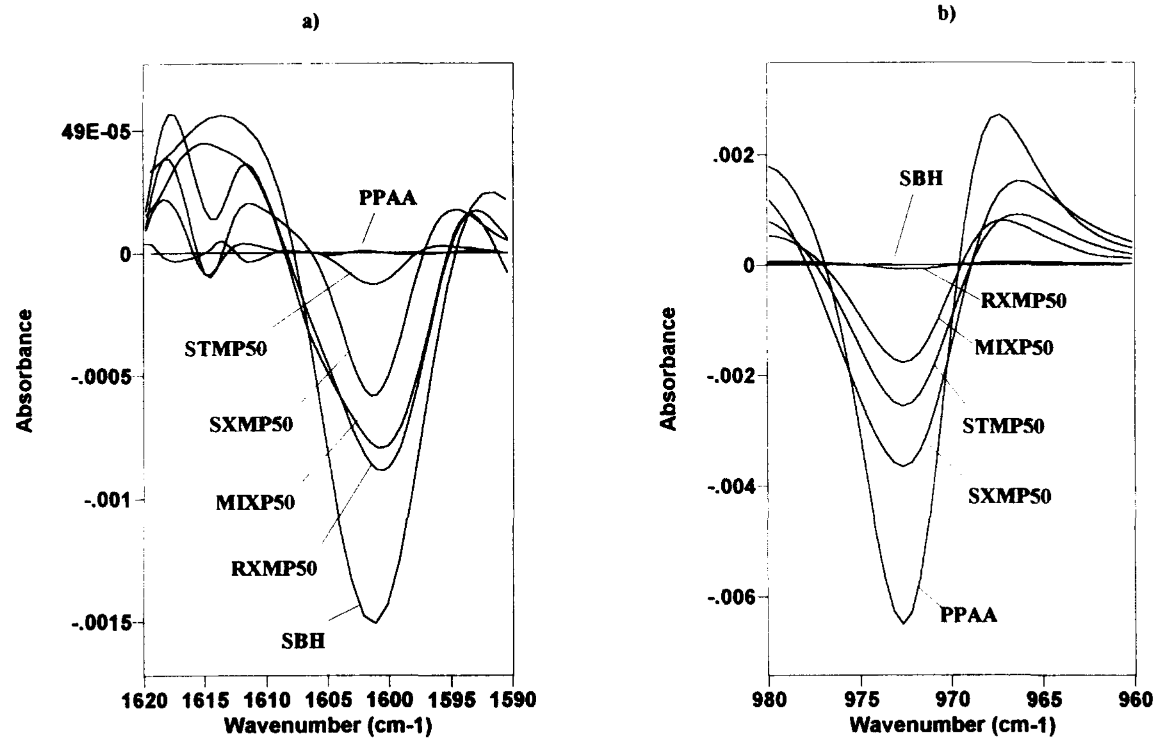

Figure 4 The second derivative spectra of MIXP50 and its fractionation products

toluene-soluble fractions of COPP50 and MIXP50 (i.e. for STCP50 and STMP50) are similar to the spectrum of PPAA, but some low-intensity bands characteristic for SBH can also be observed (*Figure 2*). The differences concern mainly the C=O ester and acid bands (*Table 1*, nos. 11 and 12). However, it can be noticed that, in the case of STCP50 and STMP50, the total area of this band is about 20 times lower than that of SBH; the absolute values of the band areas are very small and thus calculations may be erroneous. By using curve-fitting calculations the bands at 1761, 1737 and 1699 cm^{-1}, assigned to aliphatic–aromatic, aromatic–aromatic and associated C=O ester groups respectively, were found for STCP50. The presence of the band attributed to associated C=O ester groups may confirm the formation of the hydrogen bonds in STCP50. Curve-fitting calculations obtained for STMP50 show that, apart from the bands characteristic for aliphatic–aromatic and aromatic–aromatic groups, another band with relatively high intensity appears arising from associated acid groups.

In order to determine the relative amounts of SBH and PPAA in the products the second derivative spectra were used. The method for calculating the second derivative spectra was described previously[3]. This time it was found that the second derivative of the band at 1600 cm^{-1} characteristic for SBH aromatic ring vibrations exhibits maximum, whereas for PPAA the second derivative at this wavenumber is equal to zero (*Figure 3a* and *Figure 4a*). For PPAA it was found that the second derivative at 973 cm^{-1} reaches a maximum, whereas for SBH it equals zero (*Figure 3b* and *Figure 4b*). This allows us to use the 'baseline-to-peak' technique.

Thus the second derivative at 1600 cm^{-1} may correspond to the content of SBH in the products whereas the second derivative at 973 cm^{-1} can be used to determine the content of PPAA in the products. The ratios of the second derivatives at 973 and 1600 cm^{-1} are shown in *Table 2*. As can be seen, the calculated ratios of the second derivative at 1600 and 973 cm^{-1} indicate that only slight amounts of SBH are present in STCP50. This means that in this fraction the grafted chains of SBH on PPAA are very short. The presence of a small amount of aromatic structure in STMP50 may result from extraction by toluene of short-chain oligomers of SBH forming hydrogen bonds with PPAA.

The spectra of fractions soluble in xylene (SXCP50 and SXMP50) exhibit the bands characteristic for SBH and PPAA (*Figure 5*). Curve-fitting calculations indicate that in the case of SXCP50 higher amounts of unreacted acid groups appear than for SXMP50 (*Table 1*, nos. 9 and 10). On the other hand, in the SXCP50 sample, there is higher amount of aliphatic–aromatic ester groups which confirms the grafting of some acid groups in PPAA with the SBH monomers. In the case of SXMP50 certain amounts of associated ester groups can be observed, which confirm the presence of hydrogen bonds in the sample.

The intensity ratios of the second derivatives at 973 and 1600 cm^{-1} (*Table 2*) may indicate that in SXMP50 and SXCP50 there is about 3.5 times more SBH than in the case of the fraction soluble in toluene. Slightly lower amounts of SBH can be observed for SXMP50 than for SXCP50.

The spectra of the insoluble fractions (RXCP50 and RXMP50) are not identical to that of SBH (*Figure 6*). In RXMP50, bands characteristic for PPAA are poorly visible. The calculated intensity ratio of the second derivatives at 1600 and 973 cm^{-1} (*Table 2*) indicates that only slight amounts of PPAA are present in RXMP50, in contrast to RXCP50, for which this ratio is slightly higher than for COPP50. Also a difference in the shape of the band in the 1850–1650 cm^{-1} region can be noticed. This band observed for RXMP50 is broader than for RXCP50. Curve-fitting calculations indicate that in both cases some amounts of unreacted acid groups are present (*Table 1*, nos. 7 and 8).

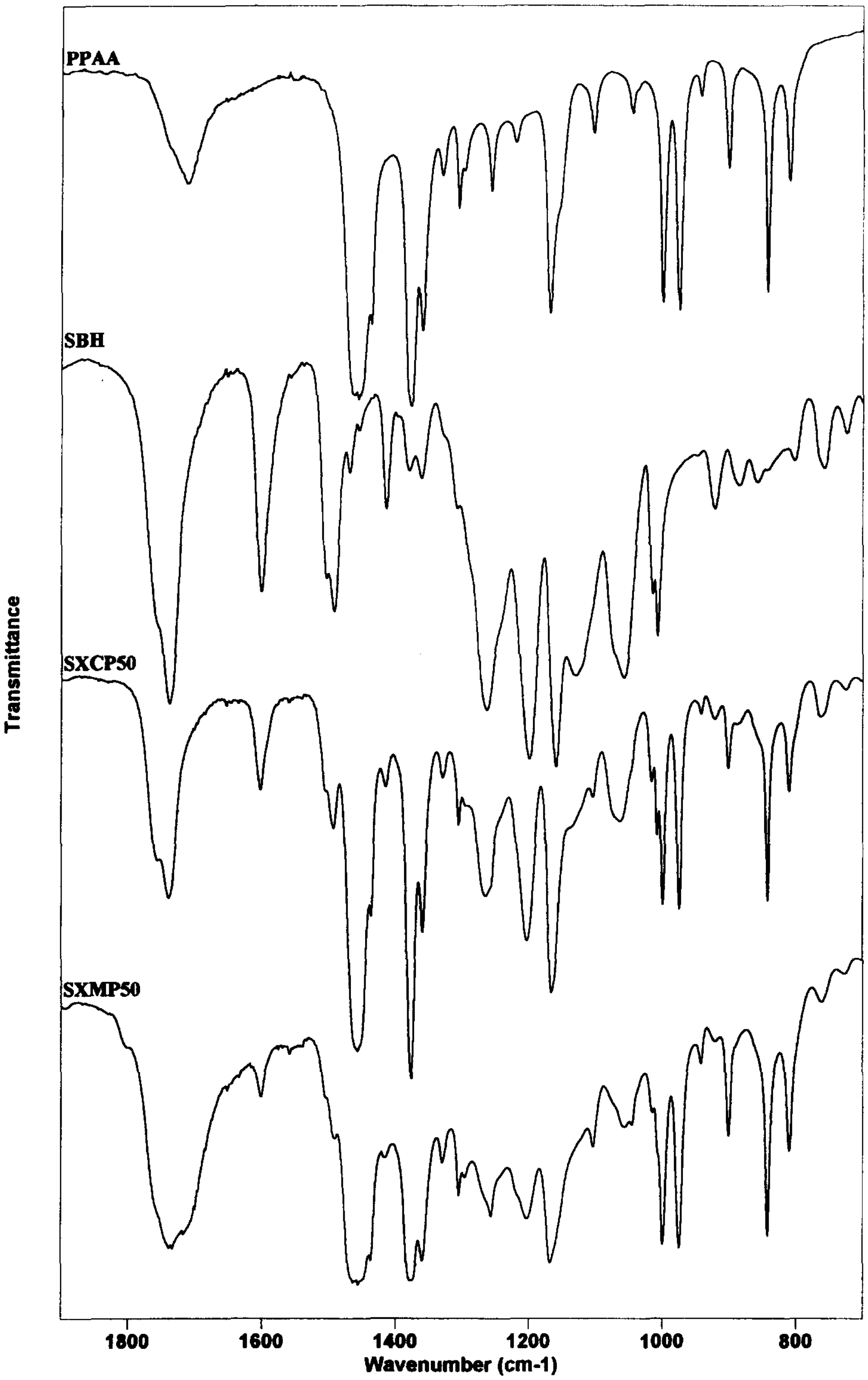

Figure 5 *FT*i.r. spectra of the fractions soluble in xylene

The areas of these bands are larger than that obtained for SBH.

It may be concluded that, during the reaction of PPAA with the monomers from which the polyester SBH was made, grafting of PPAA took place. This was confirmed by the structure of the grafted copolymer fractions which consisted of the both components, i.e. PPAA and SBH. The solubility of the fractions depends on the amount of SBH being grafted onto PPAA. In the case of the mixtures of PPAA and SBH polymer, fractionation leads to almost pure components. Small amounts of the other component in some fractions may result from the presence of hydrogen bonds between acid groups of PPAA and short-chain oligomers of the SBH polymer, thus making an efficient separation difficult.

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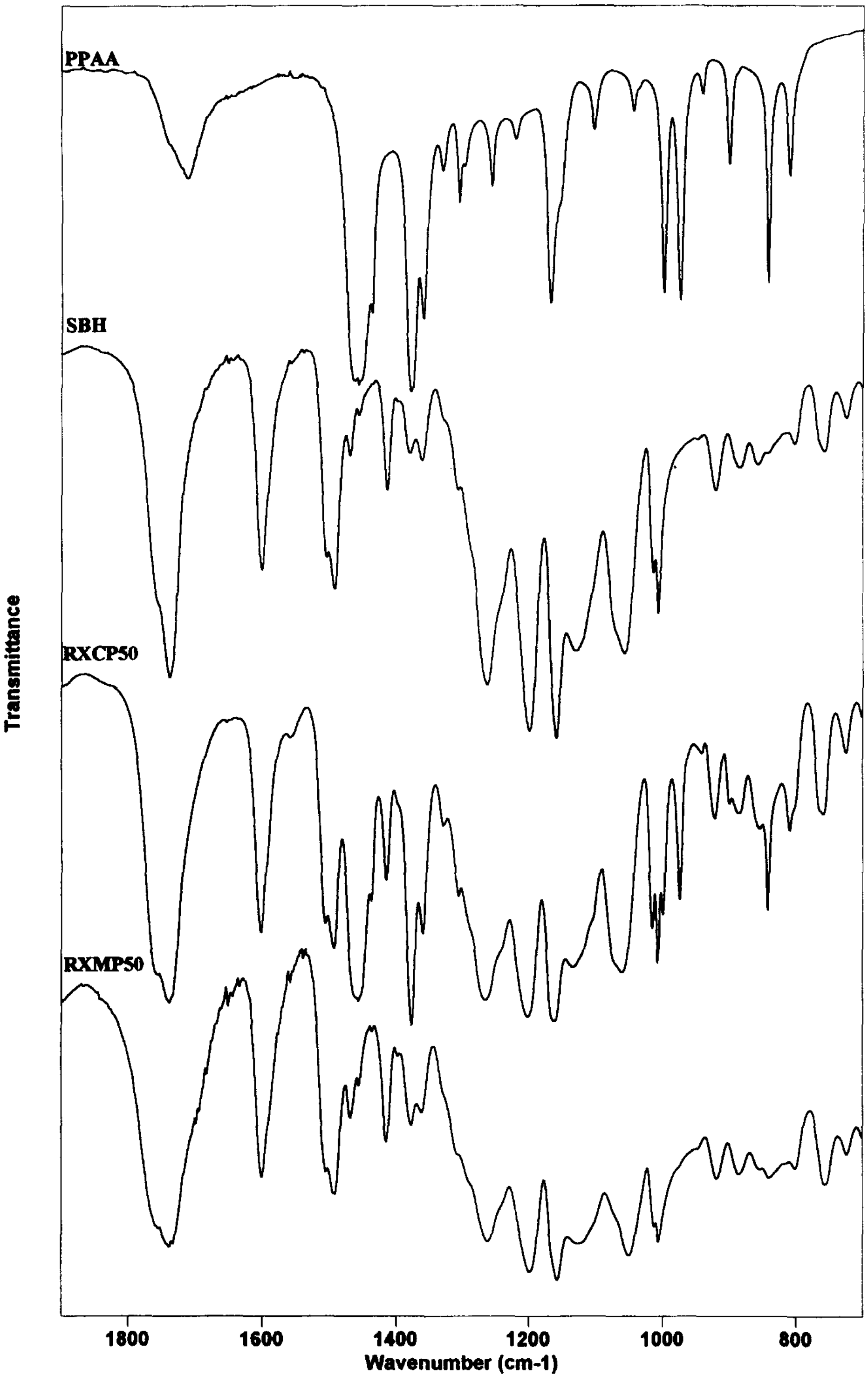

Figure 6 *FT*i.r. spectra of the fractions insoluble in xylene

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