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AN INFRARED SPECTROSCOPICAL STUDY OF GRAFTED PA COPOLYMER†

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Abstract We report a characterization of the graft copolymer of PA with polybutadiene by IR spectroscopy. The data obtained have been analyzed to clarify the band assignment, the structure of the polymer, its stability and the effect of different dopants. Also stretched films have been analysed with polarized light.

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A novel form of soluble polyacetylene (PA) has been prepared as described[1]. The existence of this grafted copolymer PA-polybutadiene (PB), is of interest because it presents an unusual opportunity to study homogeneous films with different cis/trans content.

The spectrum of this copolymer (Fig.1) shows all the bands of both PA and PB with the exception for a new band at 1377 cm^{-1} (CH_3 deformation) and for the spectral variations in the CH stretching region reported in Fig.2, both due to the grafting. The IR bands of the PA-PB film can be assigned (Table I) by comparing the data of the present work (PA-PB copolymer, activated PB and PB) with those previously reported for highly stretched samples of PA[2]. We also report (Fig.3) the dopant (I_2, Br_2) induced bands (difference spectra). These spectra are very similar to those of ref.2. Of particular interest the difference of the relative intensities of the bands originated with different dopants. While

there is no evidence of the reaction of I_2 with the polymers, Br_2 adds to both PA and PB giving rise to two C-Br stretching bands at 630 and 549 cm^{-1} respectively. By following the time dependence of the band intensities in iodine-doped spectra a quick releasing of I_2 and a gradual oxidation of PA are observed. These degradative effects are shown in Fig.4, where the cis-trans isomerisation of PA after some doping cycles is also apparent. A complete degradation of the polymeric chains is observed in a few minutes by warming up to 170°C.

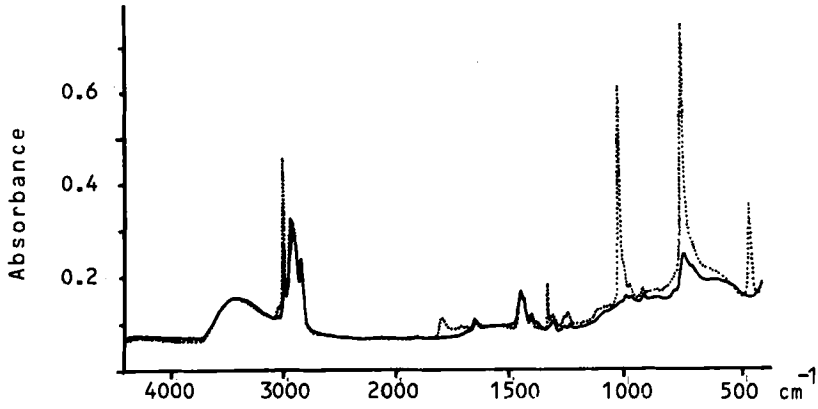

FIGURE 1 - IR spectra of PB matrix activated with the catalyst (——) and after polymerization of C_2H_2 (....) .

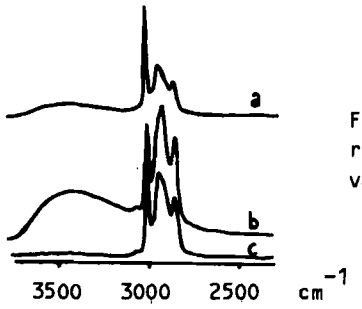

FIGURE 2- Details of the CH stretching region for PA-PB copolymers (a), activated PB (b) and PB (c) spectra.

TABLE I : Observed IR absorption bands (cm^{-1})

PA-PB copolymers	molecule	Assignment mode	group
4290 (+)	PA trans	(3011+1296)	
3444 vbr		O-H stretching	O-H··O
3057 (+)	PA cis	C-H " B_{1u}	
3044 (+)	PA cis	" " B_{3u}	-CH=CH-
3009 (++)	PA trans	" " B_u	
	PB	C-H stretching	
2942 ms	PB	" "	$-CH_2-C=$
2920 sh	PB	" "	$-CH_2-$
2851 m	PB	" "	" $"_2$
1905 (+)	PA trans	(1014+915 R)	
1800 (+)	PA cis	(1328+448)	
1690 (+)	PA cis	(1247+448) ?	
1656 w	PB	C=C stretching	-CH=CH-C-
1640 vbr		O-H in plane def.	O-H··O
1494 vvw	?		
1452 mw 1435 sh	PB	C-H bending	$-CH_2-$
1405 w	PB	C-H in plane def.	$-C=CH_2$
1377 vw	(grafting)	C-H bending	$-CH_3$
1328 (+)	PA cis	C-H in plane def. B_{1u}	
1310 w	PB	" " " "	-CH=CH-
1292 (+)	PA trans	" " " " B_u	
1260 w	PB	skeletal	
1242 (++)	PA cis	C-H in plane def. B_{3u}	
	PB	skeletal	
1110 (++)	PA cis	C-C stretching ?	
1090 w,br	PB	skeletal	
1020 sh	PB	"	
1013 s, (+)	PA trans	C-H out of plane def. A_u	
994	PB	" " " " "	$-CH=CH_2$
970 sh	PB	" " " " "	-CH=CH-trans
910 vw	PB	CH_2 " " " "	$-CH=CH_2$
743 (++) br	PA trans	defects	
	PA cis	C-H out of plane def. B_{2u}	-CH=CH- cis
	PB	" " " " "	
	PA trans	defects	
650 vbr		-O-H torsion	O-H··O
448 (+)	PA cis	C-C-C deformation B_{1u}	

Intensity (+) or position (++) depends on cis/trans ratio.

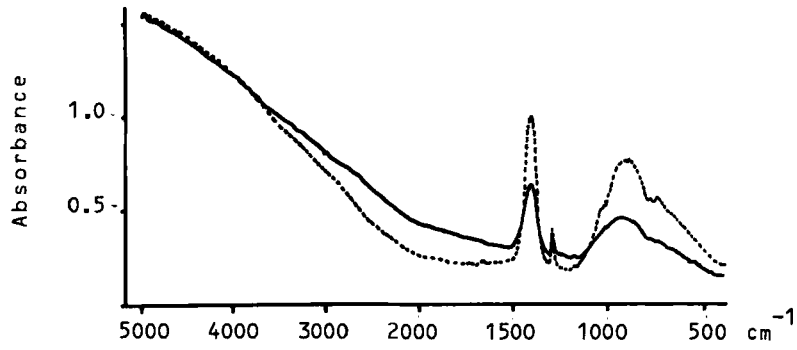

FIGURE 3 - Difference spectra of doped and undoped PA-PB copolymers: Bromine (——), Iodine (....) .

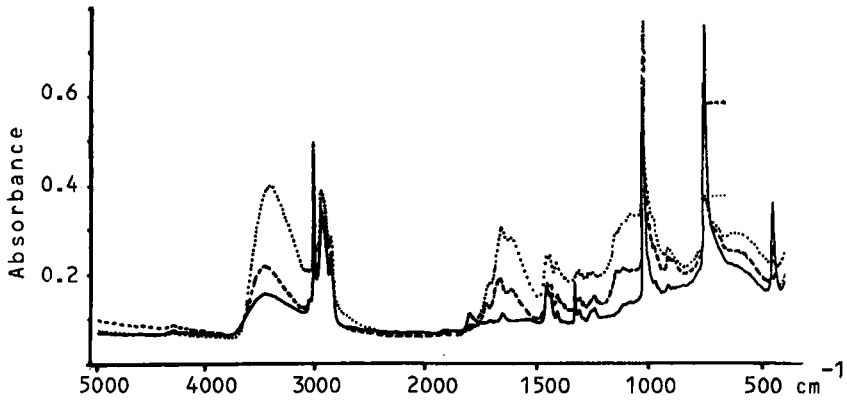

FIGURE 4 - Infrared spectra of PA-PB before (——), after one (---) and four (....) cycles of doping with iodine.

By stretching these films, while no dichroic effect is observed for PB, the dichroic ratios of the very intense defect-induced modes at 5000 and 1400 cm^{-1} are indicative of a preferred allignment of the PA chains along the stretching direction.

References

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