

Polarized FTIR Photoacoustic Spectroscopy on Blends of Thermoplastic Poly(ether-urethanes) with Modified Polypropylenes

KLAUS-JOCHEN EICHHORN,¹ IRENE HOPFE,¹ PETRA PÖTSCHKE,¹ PAVEL SCHMIDT²

¹ Institute of Polymer Research Dresden e.V., Hohe Str. 6, D-01069 Dresden, Germany

² Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 16206 Prague 6, Czech Republic

Received 11 September 1998; accepted 8 July 1999

ABSTRACT: Polarized Fourier transform infrared (FTIR) transmission and attenuated total reflection (ATR) spectroscopy are well-known powerful tools to determine the orientation function of polymer materials. Both methods demand a special sample preparation. In our present studies, we used polarized FTIR photoacoustic spectroscopy (PAS) to determine the orientation function of real products from polymer processing without special preparation. We compare the results with those obtained with polarized FTIR transmission spectroscopy. It is demonstrated that polarized FTIR–PAS is useful to describe differences in the orientational behavior of hard and soft segments of thermoplastic poly(ether-urethane) in different elongated blends with common polypropylene and polypropylene grafted with maleic anhydride. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1194–1204, 2000

Key words: polarized Fourier transform infrared photoacoustic spectroscopy; blends; thermoplastic polyurethane; modified polypropylene; molecular orientation

INTRODUCTION

Orientalional effects in polymer materials can be studied using the dichroism of orientation sensitive bands in the infrared (IR) spectra. Detailed information on the theory of infrared dichroism is available in the literature.^{1–3} The method has been successfully applied in the Fourier transform infrared (FTIR) transmission mode with linearly polarized light on uniaxially stretched polymer films, whereby the electric vector is adjusted in the parallel or perpendicular direction relative to the stretching direction. Using this technique, the orientational behavior of hard and soft segments in thermoplastic polyurethanes (TPU) and

in their blends with polyolefines has been analyzed recently.^{4,5}

For industrial applications, it is essential to get orientational data of the polymers immediately after thermoplastic processing in the given physical form without further preparation.

Photoacoustic spectroscopy (PAS) with polarized light offers some potential for a new kind of investigation. Without any special preparation, polarized PAS can be directly applied to polymeric granules, blocks, strings, sheets, and plates as received from extrusion or injection-molding processing or after being stressed by deformation in a testing machine. In this way, the preferred orientation, for example, given by machine axes or stretching direction, can be correlated with polymer structures and processing conditions. Quintanilla et al.,⁶ Jawhari et al.,⁷ Schmidt et al.,⁸ Ludwig and Urban,⁹ Jasse,¹⁰ and Choquet et

Correspondence to: K.-J. Eichhorn.

Journal of Applied Polymer Science, Vol. 75, 1194–1204 (2000)

© 2000 John Wiley & Sons, Inc.

CCC 0021-8995/00/091194-11

al.¹¹ report quantitative measurements and measurements with polarized light using the photoacoustic principle. The applicability criteria of polarized FTIR-PAS are similar to those of FTIR attenuated total reflection (ATR) spectroscopy.¹² It should be considered that we have in PAS a larger penetration depth than in ATR; more bulk material can interact with the infrared (IR) light. No structural information can be obtained from PA spectra of samples, which are optically opaque and thermally thin; the reasons are explained in the PAS fundamentals.^{13,14}

In the present studies, we investigated the orientation of polymer components in different blends of a TPU with common and with modified polypropylene (PP) after processing and, in some cases, after subsequent mechanical stretching. TPU and common PP form immiscible blends of extremely low compatibility. In order to improve the dispersity, stability, and properties of the blends, PP was grafted with maleic anhydride (MSA). The effect of this modification on the orientational behavior of TPU in the reactive compatibilized blends was also studied by polarized PAS.

EXPERIMENTAL

Polymers and Blends

A thermoplastic polyurethane elastomer with a shore hardness of 95 A (TPU; Elastollan @1195A, Elastogran GmbH) was used as the matrix. The dispersed phase consisted of polypropylene (PP; Novolen @ 1127 MX, BASF AG).

The thermoplastic polyurethane was a segmented block copolymer consisting of hard segments and polyether soft segments. The polypropylene was a homopolymer [MFR 230/2.16 = 8 g/(10 min)] recommended for flat-sheet die extrusion.

Grafting of PP

The grafting of PP with maleic anhydride (MSA) was done using a corotating, intermeshing, twin-screw extruder (ZSK 30, Werner & Pfleiderer) with a screw configuration adapted for grafting. A master batch of PP granules, 0.5 wt % di-*tert*-butyl-peroxide (Trigonox B, Peroxid-Chemie) and 2.0 wt % MSA (Merck) was fed to the extruder. A melt temperature profile from 180 to 210°C, an output of 6 kg h⁻¹, and a screw speed of 150

min⁻¹ were used. The grafted MSA-content was determined by quantitative IR spectroscopy using the intensity of the absorption band at 1792 cm⁻¹. It was found to be 0.6 wt %.

Blend Preparation

Blending of the components was done by melt-mixing in a ZSK 30 extruder. The screw configuration was adapted for the TPU-polypropylene blend system. Prior to blending, the thermoplastic polyurethane was dried for at least 3 h in vacuum at 100°C. The composition of the blend was 80 wt % TPU-20 wt % polypropylene or grafted polypropylene. The melt temperature was 210°C, the screw speed was 150 rpm, and the throughput was 10 kg/h. The residence time was about 50 s.

Injection Molding

Injection-molding was done by use of a Battenfeld 500/200 machine to produce S2 specimens for the tensile test according to DIN 53504 for elastomers (dumbbell-shaped, 2-mm thickness, 75-mm overall length, 25-mm gauge length, and 4-mm width). The residence time was up to 5 min at a maximum melt temperature of 210°C. The injection pressure was about 70 bar, and the cycle time 30 s. The specimens were tested after annealing for 24 h at 100°C.

Preparation of Mechanically Stretched Specimens for Polarized FTIR-PAS

Some injection-molded specimens were stretched at about 5, 150, or 200%. Inside the stretching machine, the stretched specimens were fixed in the elongated state with their backside on a circular brass plate (10 mm) with adhesive LOC-TITE 401. Then we cut exactly the projected parts of the sample outside of the brass plate and transferred this photoacoustic sample into the photoacoustic cell. The sample was placed precisely in a defined position of its processing or stretching direction.

METHODS

Polarized FTIR-PAS measurements were performed on a Bruker IFS 66v/S using the MTEC 200 photoacoustic cell (Ames, IA). For polarization of IR radiation, a KRS-5 wire grid polarizer (SPECAC) was inserted immediately in front of

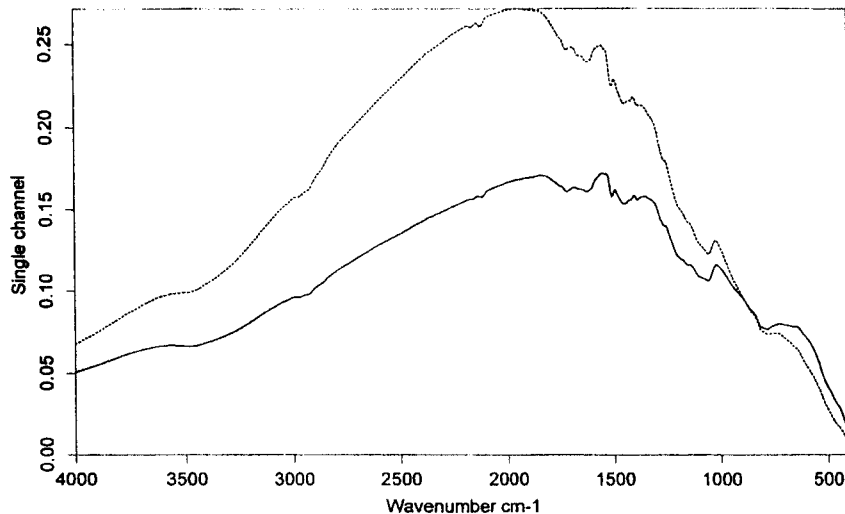


Figure 1 Polarized PA background spectra of carbon black sample (2.2 kHz) after 1 h He purge: full line, with polarizer parallel (0° , \parallel); dotted line, with polarizer perpendicular (90° , \perp).

the cell. Two quantitative measurements for the background (carbon black; Fig. 1) and the sample were performed by rotating the polarizer, first with parallel (\parallel) 0° polarization and then with

perpendicular (\perp) 90° polarization of the electric vector, with the photoacoustic cell purged with He for at least 1 h before the beginning of the measurement.

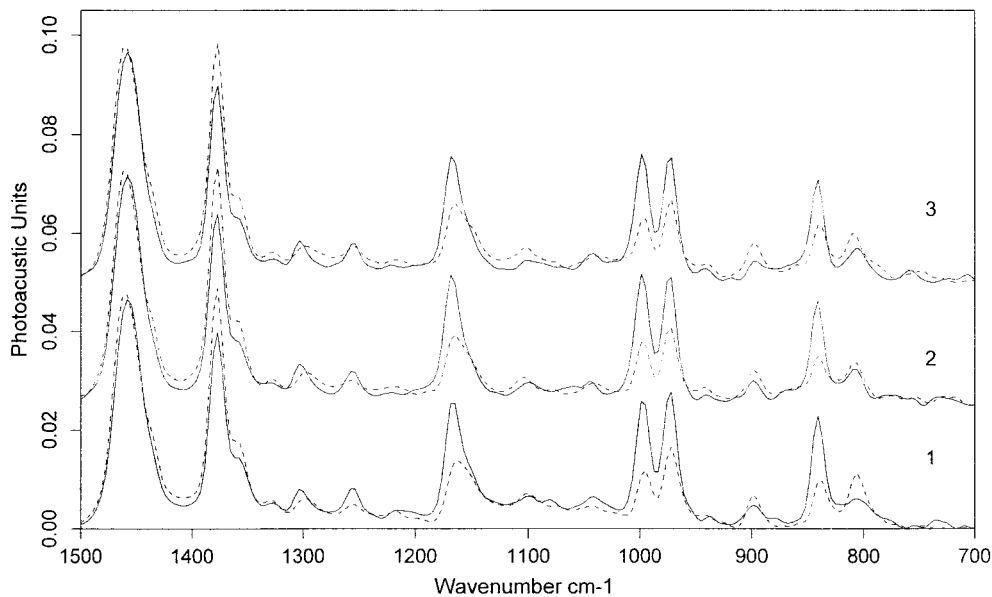


Figure 2 Different techniques of measurement of polarized PA spectra of oriented polymers (demonstrated on a stretched PP sample): (1) maintaining the sample with a defined direction of orientation in the cell and rotating the polarizer [(—) parallel (0° , \parallel); (- - -) perpendicular (90° , \perp)]; (2) maintaining the polarizer horizontal within the spectrometer and rotating the sample in the cell [(—) parallel (0° , \parallel); (- - -) perpendicular (90° , \perp)]; (3) maintaining the polarizer vertical within the spectrometer and rotating the sample in the cell [(—) parallel (0° , \parallel); (- - -) perpendicular (90° , \perp)].

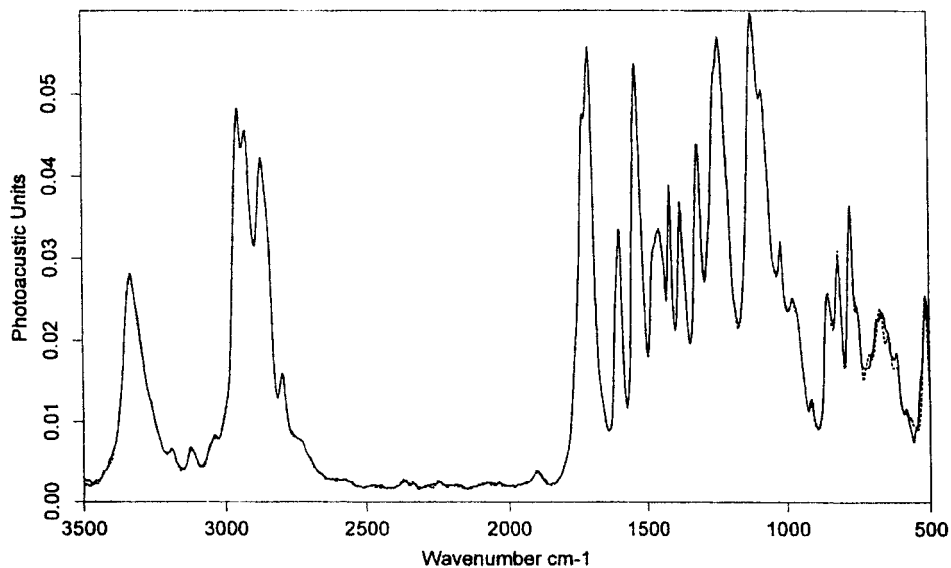


Figure 3 Reproducibility of the polarized PAS experiments [TPU-PP-*g*-MSA, injection-molded bar, 5% elongated, and perpendicular (90° , \perp): (—) measured at t ; (---) measured at $t + 30$ days.

All the following PA spectra of our samples were ratioed to the corresponding parallel and perpendicular carbon black spectra.

The mirror velocity was 0,139 cm/s (2.2 kHz), and the resolution was 4 cm^{-1} . Two kinds of experiments were performed on a series of samples with different orientations to test if the light polarization was degraded by the focusing/turning mirror of the PA cell, as follows: (1) rotating the sample in the cell

while maintaining the polarizer horizontal and vertical as well, and (2) maintaining the sample with a defined direction of orientation in the cell and rotating the polarizer from the corresponding parallel (0°) position to the perpendicular (90°) position.

So, we have proven both the rotation of the sample with the constant position of the polarizer, and the constant position of the sample rotating the polarizer. The results were practically identi-

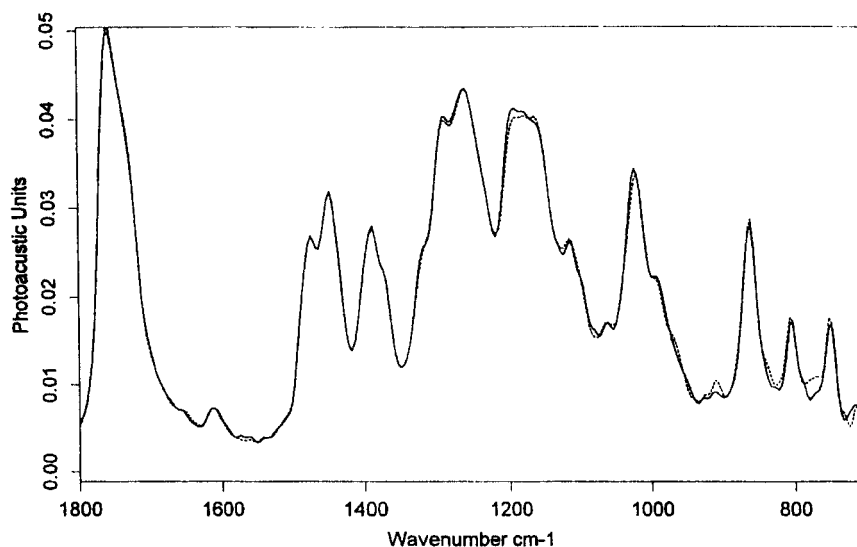


Figure 4 Polarized PA spectra [(—) parallel (0° , \parallel); (---) perpendicular (90° , \perp)] of the adhesive LOCTITE 401, used for fixation of the stretched bars on PAS target.

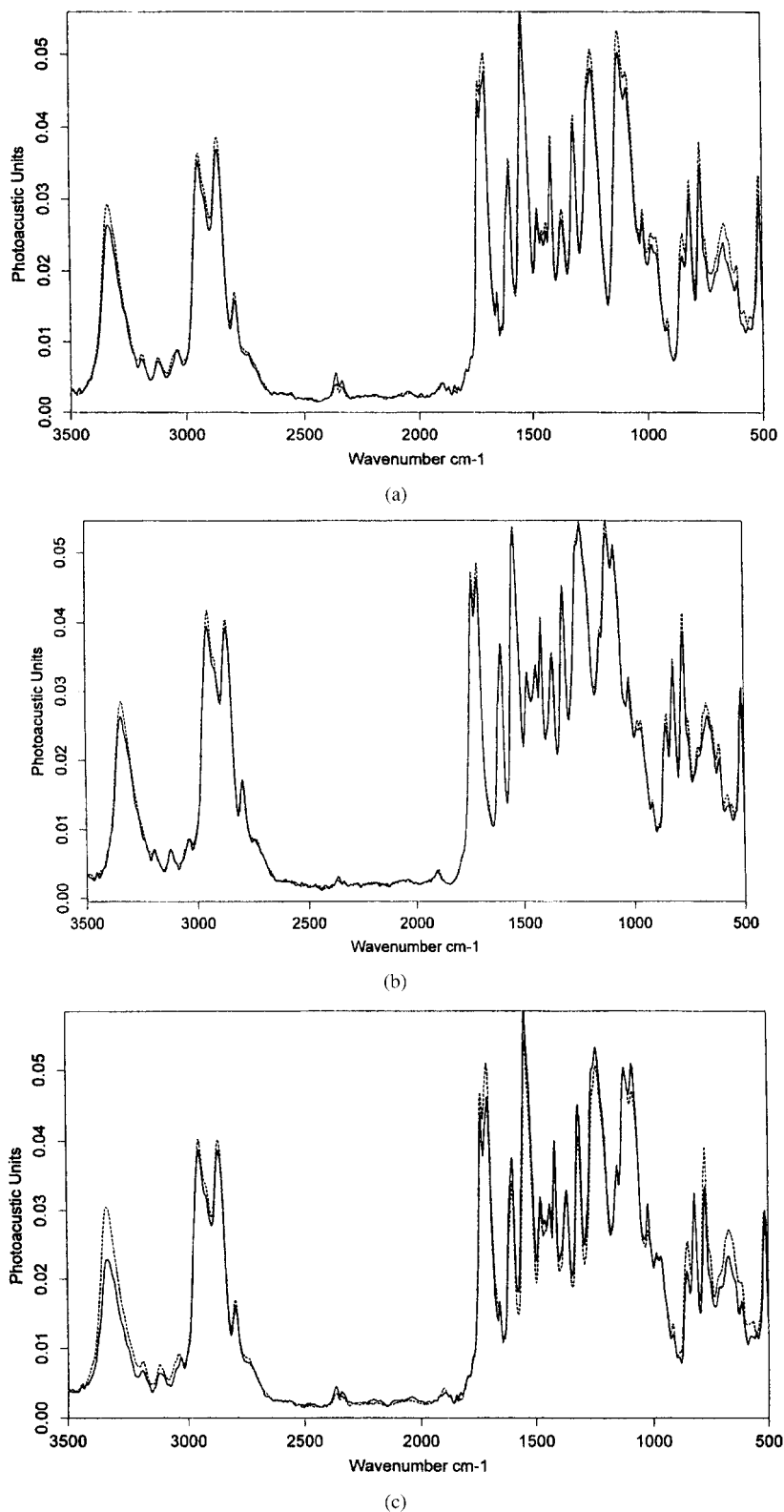


Figure 5 Polarized PA spectra [(—) parallel (0° , \parallel); (- - -) perpendicular (90° , \perp)] of pure poly(ether-urethane): (a) extruded granule; (b) injection-molded bar, 5% elongated; and (c) injection-molded bar, 50% residual elongation after stretching up to 200% and relaxation.

Table I PAS Dichroic Ratios R and PAS Orientational Functions f_{PAS} Calculated for Selected TPU Bands from the PA Spectra of Pure Poly(ether-urethane)s with Different Elongation

IR Band (cm^{-1})	Extruded Granule		Injection-Molded Bar (5% Elongation)		Uniaxially Stretched (50% Residual Elongation after Stretching)	
	R	f_{PAS}	R	f_{PAS}	R	f_{PAS}
3334 \perp Hard segment	0.89	0.08	0.99	0	0.76	0.18
1735 \perp	0.96	0.02	0.93	0.04	0.82	0.13
1706 \perp	0.95	0.03	0.99	0	0.88	0.09
1316 \parallel Hard + soft segment	0.98	0	0.98	0	1.16	0.05
1115 \parallel Soft segments	0.86	-0.05	0.86	-0.05	0.87	-0.04
1081 \parallel	1.07	0.02	1	0	1.05	0.02

cal. An example is shown in Figure 2. We preferred the second type of work, as in this case [case (2) above], it is not necessary to open the photoacoustic cell between the two measurements, which could possibly change the response of the photoacoustic detector.

Figure 3 documents the reproducibility of our polarized PA spectra. The two spectra, measured for the same sample at different times (the sample being removed from the PA cell between measurements and realigned), are nearly identical.

The PA spectra of a cured sample of the pure adhesive used for fixing the stretched samples were also recorded at 0 and 90°. As expected, we found no dichroic behavior of the adhesive (Fig. 4). So, we excluded the influence of possible residual adhesive contaminants from the fixing procedure on the dichroic spectra of the polymers.

Determination of the Photoacoustic Dichroic Ratios and Orientation Functions

The aim of our work was to get information about the orientation of the pure polymers and the individual components in the blends from the PA spectra. The intensities of the photoacoustic signals of the orientation sensitive bands used were in the linear range (also see the Results and Discussion section). So, we integrated the structurally dependent PA bands like absorbance bands in transmission spectra. The orientation of the polymers and individual components in our blend samples was investigated by means of the TPU bands between 1650–1800 cm^{-1} (carbonyl stretching vibrations), at 3334 cm^{-1} (NH stretching vibration), and at 1316 cm^{-1} (C—N), 1115 cm^{-1} (C—O—C) and 1081 cm^{-1} , respectively, and of the PP band at 1379 cm^{-1} (methyl deformation

Table II PAS Dichroic Ratios R and PAS Orientational Functions f_{PAS} Calculated Using the δCH_3 Deformation Band (\perp) at 1376 cm^{-1} for Common PP and MSA-grafted PP (PP-*g*-MSA) Samples with Different Elongations

Sample	Extruded Granule		Injection-Molded Bar, Uniaxially Stretched and Fixed at an Elongated Position					
	R	f_{PAS}	5% Elongation		150% Elongation		200% Elongation	
	R	f_{PAS}	R	f_{PAS}	R	f_{PAS}	R	f_{PAS}
Common PP (PP1127 MX)	0.91	0.06	0.84	0.12	0.51	0.39		
MSA-grafted PP (PP1127 MX- <i>g</i> -MSA)	0.85	0.10	0.87	0.09			0.48	0.42

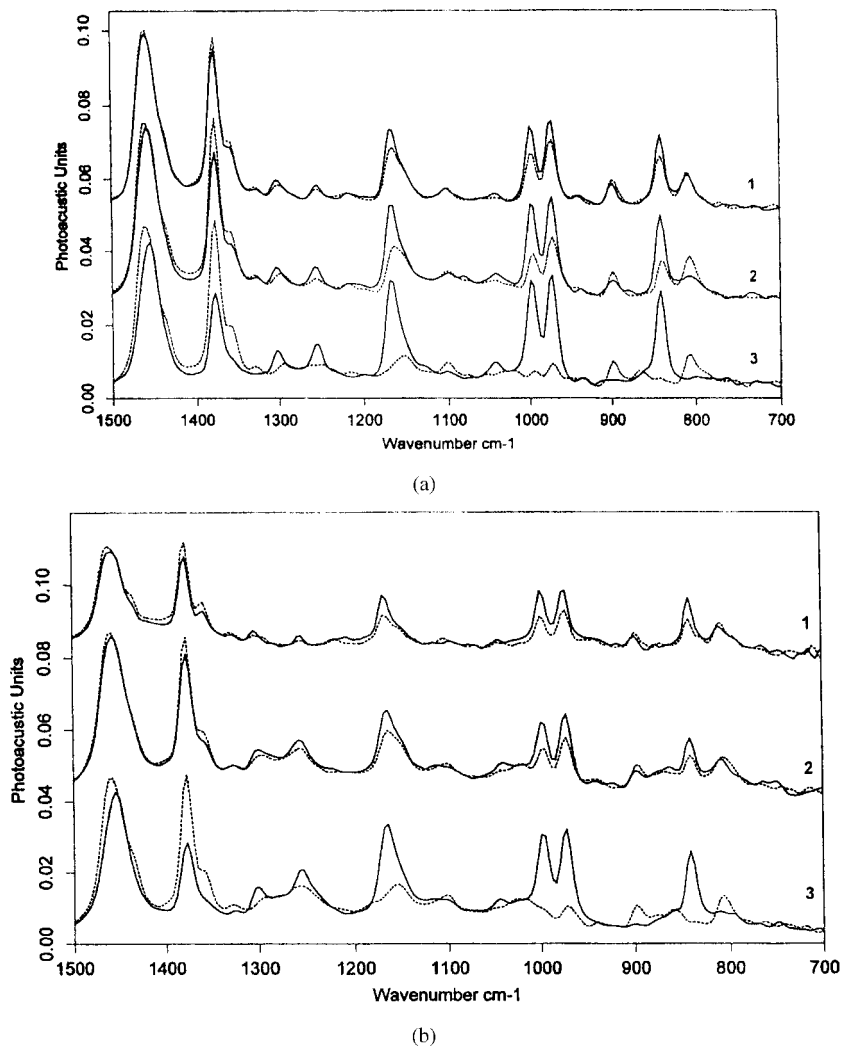


Figure 6 (a) Polarized PA spectra [(—) parallel (0° , \parallel); (- - -) perpendicular (90° , \perp)] of the common PP: (1) extruded granule; (2) injection-molded bar, 5% elongated and fixed; and (3) injection-molded bar, 150% elongated and fixed. (b) Polarized PA spectra (—) parallel (0° , \parallel) and (- - -) perpendicular (90° , \perp) of PP-g-MSA: (1) extruded granule; (2) injection-molded bar, 5% elongated and fixed; (3) injection-molded bar, 200% elongated and fixed.

vibration).⁴ The direction of the dipole transition moments of the carbonyl, NH stretching, and methyl deformation vibrations is located in a perpendicular (\perp) direction relative to polymer chain axis, and the direction of the others is located in a parallel (\parallel) direction. Assuming an uniaxial chain alignment in the machine (or stretching) direction, a photoacoustic orientation function f_{PAS} can be calculated from the polarized PA spectra in the same way as described in the literature^{12,15,16} for transmission spectra.

Based on Fraser's function¹⁷ for the perpendicular absorption bands ($f_{\text{PAS}} \equiv f_{\perp}$) and for the parallel ones ($f_{\text{PAS}} \equiv f_{\parallel}$), eqs. (1) and (2) were applied, as follows:

$$f_{\perp} = -2(R - 1)/(R + 2) \quad (1)$$

$$f_{\parallel} = (R - 1)/(R + 2) \quad (2)$$

where the dichroic ratio is defined as $R = A_{\parallel}/A_{\perp}$, and A_{\parallel} and A_{\perp} are, in our experiments, the absorbance-like photoacoustic signal intensities in the polarization spectra taken with light polarized parallel and perpendicular to the machine (or stretching) direction, respectively. Note that the well-known Hermans orientation function f^{H} ¹⁸ is defined as

$$f = \frac{3\langle \cos^2\Theta \rangle - 1}{2} \quad (3)$$

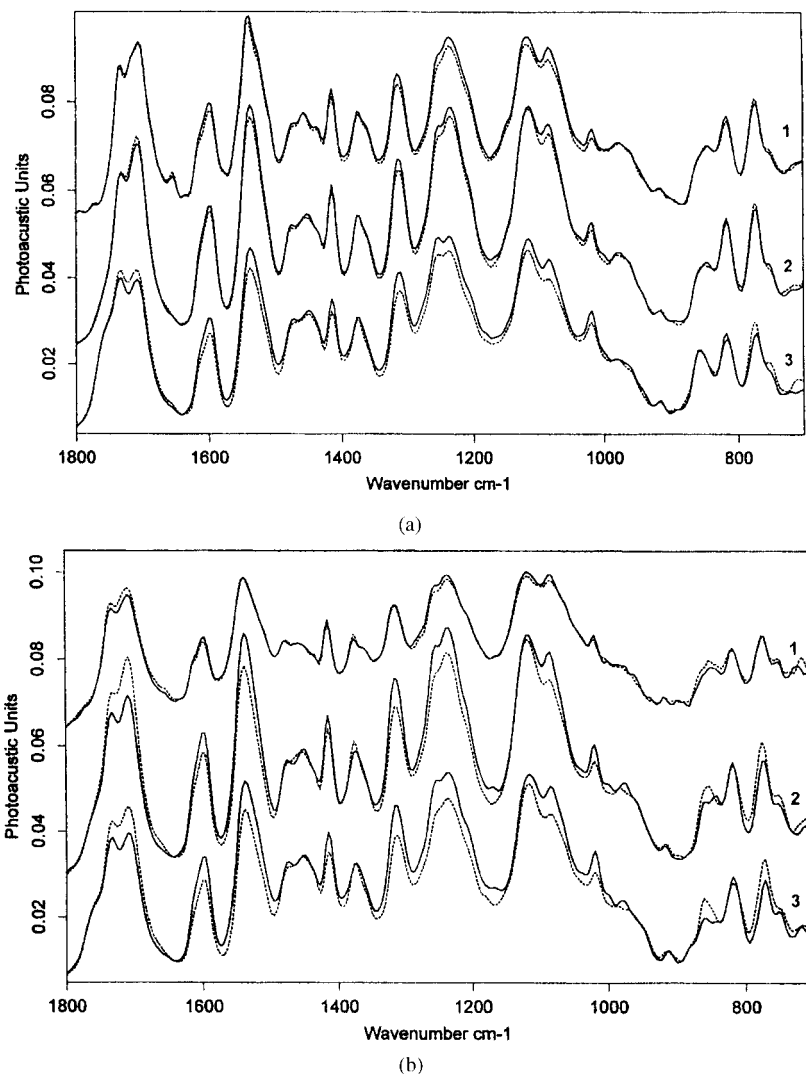


Figure 7 Polarized PA spectra (—) parallel (0° , \parallel) and (---) perpendicular (90° , \perp) of (a) the 80/20 TPU–common PP blend and (b) the 80/20 TPU–PP-*g*-MSA blend: (1) extruded granule; (2) injection-molded bar, 5% elongated and fixed; (3) injection-molded bar, 200% elongated and fixed.

where Θ is the angle between the polymer chain or chain segment axis and a preferred direction (machine or stretching direction).

Therefore, the following threshold values are possible: $f = 1$, fully oriented in the preferred direction; $f = 0$, no orientation; and $f = -\frac{1}{2}$, oriented perpendicular to the preferred direction.

RESULTS AND DISCUSSION

Application of Polarized PAS for the Determination of Orientation in Polymers

The point is that, normally, the optical absorption measured in the IR is the basis for the calculation

of the IR dichroic ratios and the orientation functions, respectively. If PAS is applied, the obtained photoacoustic signal depends on the optical and thermal properties of the sample. Signal saturation is a particular feature of PAS, which occurs if thermal diffusion length exceeds the optical penetration depth¹⁹; but if thick polymer specimens (as in our case) are examined in spectral regions far from their strong absorptions, there is a linear relation between the photoacoustic signal and absorbance,¹³ at least in the optically opaque and thermally thick case. Considering oriented samples, the polarization dependence of the absorptivity (i.e., dichroism) will result in a polarization dependence of the PAS signal.¹³ For polarization

Table III PAS Dichroic Ratios R and PAS Orientational Functions f_{PAS} Calculated for the TPU Component (Selected Bands)

IR Band (cm^{-1})	Injection-Molded Bar, Uniaxially Stretched and Fixed at an Elongated Position					
	Extruded Granule		5% Elongation		200% Elongation	
	R	f_{PAS}	R	f_{PAS}	R	f_{PAS}
3334 \perp^{a}	1.02	-0.01	0.92	0.05	0.85	0.11
(Hard segments) ^b	0.85	0.11	0.74	0.19	0.69	0.23
1734 \perp^{a}	1.17	-0.11	1.04	-0.02	0.94	0.04
\perp^{b}	1.33	-0.20	0.97	0.02	0.96	0.03
1706 \perp^{a}	1.13	-0.08	0.95	0.03	0.90	0.07
\perp^{b}	0.88	0.08	0.75	0.18	0.70	0.22
1316 \parallel^{a}	1.00	0.00	0.99	0.00	1.00	0.00
(Hard + soft segments) ^b	1.08	0.03	1.26	0.08	1.36	0.11
1115 \parallel^{a}	1.00	0.00	0.88	-0.04	1.09	0.03
(Soft segment) ^b	1.14	0.04	0.98	0.00	1.15	0.05
1081 \parallel^{a}	1.23	0.07	0.81	-0.07	1.26	0.08
\perp^{b}	1.16	0.05	1.34	0.10	1.00	0.00

^a 80/20 TPU–common PP blend.^b 80/20 TPU–MSA-grafted PP blend.

measurements, it is also advisable to choose orientation-sensitive bands of weak or medium intensity to decrease the photoacoustic saturation. Such bands can be easily found, for example, in the spectra of polypropylene.¹²

The fact is that the nonlinearity of the intensities with respect to the concentration can be never fully excluded. The effect of this nonlinearity increases with the intensity of the bands.²⁰ So, we assume that the nonlinearity for the 1706 cm^{-1} band in the PA spectra of our TPU polymers and

blends is larger than for the other bands. Nevertheless, when comparing samples of different orientation, the trend of the calculated dichroic ratios is the same as for the weaker bands. So, for the bands with partial saturation, qualitative comparison is also possible at least. To our knowledge, only Krishnan et al.²¹ have published dichroic data of polymers obtained from PAS with polarized light so far. According to him, it should be possible to get at least semiquantitative orientation information by our described procedure.

Table IV PAS and Transmission Spectroscopic Orientation Functions for TPU in TPU–PP Blends with Modified PPs Calculated for Selected Bands

Orientation Function of TPU in Blend	5% Elongation			200% Elongation		
	a	a	b	a	a	b
	With PP ^d	PP ^e	PP ^f	PP ^d	PP ^e	PP ^f
	f_{PAS}	f_{PAS}	f_{Trans}	f_{PAS}	f_{PAS}	f_{Trans}
1310 cm^{-1}	-0.01	0.08	0	0	0.11	0.18
1112 cm^{-1}	-0.04	0.01	0	0.03	0.05	0.11

^a Polarized PAS on compact samples (this study).^b Rheo-optical FTIR spectroscopy (transmission) on thin films (Fischer et al.⁴).^d TPU in TPU–common PP.^e TPU in TPU–PP-*g*-MSA (0.6 wt % grafted MSA).^f TPU in TPU–PP with rubber phase (20 wt % rubber).

Pure Poly(ether-urethane)

Figure 5 shows the polarized PA spectra; in Table I, the dichroic ratios R and the PAS orientational functions f_{PAS} of the pure TPU samples are listed.

The extruded strings and the less-elongated (5%) injection-molded bars of the thermoplastic poly(ether-urethane) are nearly unoriented ($f_{\text{PAS}} \approx 0$). Weak orientation ($f_{\text{PAS}} \approx 0.1 \dots 0.2$), especially within the hard segments, could be observed in the bars that have a higher residual elongation (50%) after the stretching experiment and the following relaxation process.

Common Polypropylene (PP) and Functionalized Polypropylene (PP-g-MSA)

The PP granules and the less-elongated (5%) injection-molded bars show very weak orientation ($f_{\text{PAS}} \leq 0.1$). As expected for the fully oriented PP bars (150 and 200%), the orientation values are relatively high ($f_{\text{PAS}} \approx 0.4$).

There is no significant difference in orientation behavior between the common and the MSA-grafted PP. The results are summarized in Table II and Figure 6.

80/20 Blends of TPU with the Two PP Types

The orientation behavior of the TPU was influenced in a special way if blended with different PPs (Fig. 7; Table III).

In the granules from the extrusion process and in the less-elongated injection moldings (5%), there was only a little change compared with pure TPU (Fig. 5; Table I): Only the influence on the hard segments seems to be changed as a result of blending with both PPs; otherwise, no remarkable orientation is observed.

The following interesting effects occur if the injection-molded bars are elongated up to 200%: The TPU component, especially the hard segments, are more oriented in the blends with MSA-grafted PP ($f \geq 0.2$) than in the blends with common PP ($f \leq 0.1$). This could be a result of a better phase adhesion and compatibility between the very orientation-sensitive PP, which is, in our case, modified with polar groups (MSA). Also, more intensive interactions with the polar hard segment domains of the TPU are possible. Pötschke et al.²² reported that the better phase adhesion between the matrix and dispersed phase in TPU-MSA-grafted PE blends improves the me-

chanical properties, which are strongly influenced by the morphological properties of the material (e.g., orientation).

Comparison of the Polarized PAS with Data of Rheo-optical Transmission Spectroscopy on Similar Samples

Table IV gives a survey of the results obtained with PAS and transmission spectroscopy on similar blends which we reported recently.⁴ The rubber-phase-modified PP [TPU in TPU-PP with rubber phase (20 wt % rubber)] used in the former studies and the MSA-grafted-PP [TPU in TPU-PP-g-MSA (0.6 wt % grafted MSA)] show a similarity in their tendency to improve the interaction between the two polymer phases in PP-TPU blends.

CONCLUSIONS

Polarized FTIR-PAS spectroscopy is suitable for detecting orientation effects in polymers and polymer blends. The advantage of PAS is that the polymer specimens may be examined in the form in which they are obtained from the thermoplastic processing, as follows: extruded granules and injection-molded bars. A PAS orientation function f_{PAS} was defined, presuming a linear relation between PA intensities and absorbance. This procedure is especially useful if orientation in different elongated samples should be compared. In this case, orientational data obtained with polarized PAS give the same trend compared to ATR and transmission spectroscopy with polarized light.

With polarized PAS, we found differences in the orientation behavior of the hard and soft segments in a thermoplastic poly(ether-urethane) if blended with common or modified polypropylene and after subsequent stretching. Grafting of PP with maleic anhydride gives rise to a better orientation of the TPU hard segments in the blends.

The authors thank G. Adam (FTIR spectroscopy) and U. Reuter (mechanical testing and stretching experiments) for their helpful contributions.

REFERENCES

1. Siesler, H. W.; Holland-Moritz, K. *Infrared and Raman Spectroscopy of Polymers*; Marcel Dekker: New York, 1980.

2. Dechant, J. *Ultrarotspektroskopische Untersuchungen an Polymeren*; Akademieverlag: Berlin, Germany, 1972.
3. Read, B. E. in *Structure and Properties of Oriented Polymers*; Ward, M., Ed.; Applied Science: London, UK, 1975; p. 150.
4. Fischer, W. B.; Pötschke, P.; Pompe, G.; Eichhorn, K.-J.; Siesler, H. W. *Macromol Chem Phys* 1997, 198, 2057.
5. Siesler, H. W. *Advances in Polymer Science*, Vol. 65; Springer-Verlag: Berlin, Germany, 1984.
6. Quintanilla, L.; Podriguez-Cabello, J. C.; Jawhari, T.; Pastor, J. M. *Polymer* 1994, 35, 514.
7. Jawhari, T.; Quintanilla, L.; Pastor, J. M. *J Appl Polym Sci* 1994, 51, 463.
8. Schmidt, P.; Fernandez, M. R.; Pastor, J. M.; Roda, J. *Polymer* 1997, 38, 2067.
9. Ludwig, B. W.; Urban, M. W. *Polymer* 1997, 38, 2977.
10. Jasse, B. *J Macromol Sci, Chem* 1989, A26, 43.
11. Choquet, M.; Rousset, G.; Bertrand, L. *Can J Phys* 1986, 64, 1081.
12. Schmidt, P.; Raab, M.; Kolarik, J.; Eichhorn, K.-J. *Polym Test* 2000, 19, 205.
13. Garton, A. *Infrared Spectroscopy of Polymer Blends, Composites and Surfaces*, Hanser: Munich, Germany, 1992.
14. McClelland, J. F. *Anal Chem* 1983, 55, 89A.
15. Sahre, K.; Eichhorn, K.-J.; Reichelt, N.; Hummel, D. O. *Acta Polym* 1994, 45, 36.
16. Zebger, I.; Pospiech, D.; Böhme, F.; Eichhorn, K.-J.; Siesler, H. W. *Polym Bull* 1996, 36, 87.
17. Fraser, R. D. B. *J Chem Phys* 1958, 29, 1428.
18. Hermans, P. H. in *Contributions to the Physics of Cellulosic Fibers*; Elsevier: Amsterdam, The Netherlands, 1946; p. 138.
19. Oelichmann, J. *Fresenius Z Anal Chem* 1989, 333, 535.
20. Schmidt, P.; Novakova, J.; Roda, J.; Pastor, J. M. *Die Angew Makromol Chem* 1997, 245, 113.
21. Krishnan, K.; Hill, S.; Hobbs, J. P.; Sung, C. S. P. *Appl Spectrosc* 1982, 36, 257.
22. Pötschke, P.; Wallheinke, K.; Stutz, H. *Polym Eng Sci* 1999, 39, 1035.