

# Telechelic polyisobutylene with unsaturated end groups and with anhydride end groups

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Anhydride terminated polyisobutylene (PIB) oligomers were synthesized in a one- or two-step process from chlorine terminated oligomers. In the one-step process, chlorine functional oligomers were just heated in the presence of maleic anhydride (MA) for 12 h at 190°C without a catalyst. In the two-step process, the chlorine end functional groups were first converted by selective dehydrochlorination to isopropenylpolyisobutylene end groups with *t*-BuOK in refluxing tetrahydrofuran during 16 h. In a second step, MA was coupled to the PIB with unsaturated end groups by reacting the oligomer with MA for 12 h at 190°C. These reactions could be followed by i.r. and n.m.r. The PIB-MA obtained had a functionality between 30% and 100%. In order to study the formation of amine functionalities, the PIB-MA was reacted with diamines. The coupling gave an imide bonding.

(Keywords: telechelic; polyisobutylene; end group modification)

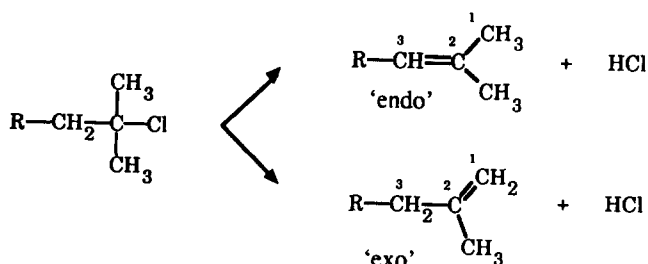
## INTRODUCTION

One interesting class of polymers is the segmented block copolymers. Some of these polymers have characteristics of thermoplastic elastomers (TPEs). In these TPEs, one segment is amorphous and has a low glass transition temperature ( $T_g$ ) while the other can crystallize and has a high melting temperature. Polyethers, with low thermal and oxidative stabilities, are mainly used for the low  $T_g$  segment in TPEs.

One segment that has the potential to combine this low  $T_g$  with good stability is polyisobutylene (PIB). In order to synthesize block copolymers containing PIB, end functional PIB oligomers (telechelics) have to be used. At present, these materials are not available with suitable end groups. Linking of the segments is normally accomplished by a condensation reaction. Therefore, the PIB should be functionalized with end groups that are reactive in a polycondensation reaction. To obtain a linear, high molecular weight polymer, these segments should be exactly bifunctional.

With anionic polymerization, it is possible to obtain well-defined end groups. This is also true for some cationic polymerizations<sup>1</sup>. With the living PIB synthesis chlorine end groups are nearly always obtained. Termination of living PIB with EtN<sub>3</sub>, pyridine and methanol gave solely chlorine end groups<sup>2</sup>. The same occurs with other nucleophiles like esters, anhydrides, ethers, ketones, dimethylsulfoxide and *N,N*-dimethylacetamide<sup>3</sup>. There are only a few exceptions. It has been shown that it is possible to link anisole to the living end<sup>4</sup>. Also, allyl end groups were introduced in one step by terminating with allyltrimethylsilane<sup>3</sup> or an allylstannate<sup>5</sup>.

The chlorine end group of PIB-Cl can be converted to obtain functional groups<sup>6,7</sup> suitable for further polymerization. By elimination of HCl from the chain end, a PIB oligomer with an unsaturated end group is obtained (PIB-U). The elimination is carried out by heating the PIB-Cl and two kinds of unsaturated groups are formed: one with a double bond inside the polymer chain at a 2,3-position ('endo') and one with the double bond outside the chain at the 1,2-position ('exo'). The exo form is preferred because it has a higher reactivity<sup>8</sup>. It can be obtained quantitatively by abstracting the HCl with a sterically hindered base such as *t*-BuOK<sup>9,10</sup> or even with EtONa<sup>11</sup>.

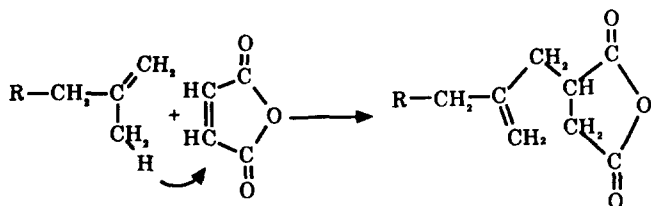


The exo double bond can be used to add a variety of compounds to the chain end<sup>12</sup>. One of the possibilities is the addition of an unsaturated anhydride group<sup>13-15</sup> by an ene reaction. With this type of reaction only one monomer is added. This anhydride group will give a telechelic that is reactive towards alcohol and amine groups. The addition of acrylic acids is not favourable as their rate of reaction of an ene type is too slow, and a radical or ionic reaction will not stop after one addition. Other possibilities for the conversion of the double bond

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are hydroboration, hydrosilation, free radical addition of thiols and reaction with chlorobenzoic acid.

The addition of maleic anhydride (MA) to PIB-U was studied by Tessier and Maréchal<sup>15,16</sup>. They used telechelic PIB as well as model compounds and analysed the products with <sup>1</sup>H n.m.r. It appeared that the MA reacted by means of an ene reaction with PIB-U.



Ene reactions are also possible with azo compounds, which are more reactive than MA<sup>17</sup> so that lower synthesis temperatures can be used. The use of this kind of reactant is not examined here.

Our aim was to study the synthesis of MA endcapped PIB, starting from the dichlorine terminated oligomers, as obtained by cationic polymerization.

## EXPERIMENTAL

### Materials

The synthesis of chlorine endcapped PIB is described elsewhere<sup>18</sup>. The MA, TiCl<sub>4</sub>, AlCl<sub>3</sub> and the solvents were obtained from Merck.

### Analytical techniques

*I.r. spectroscopy.* A Perkin-Elmer 1310 i.r. spectrophotometer and a Biorad 60 Fourier transform i.r. spectrophotometer were used for i.r. analyses of the PIB telechelics. The viscous telechelics were smeared as a thin film on one side of a NaCl plate.

*<sup>1</sup>H n.m.r.* End groups of the telechelics were studied with a Bruker 80 MHz spectrometer. Solutions of 5–10% telechelic in *d*-chloroform were used. Trimethylsilane was used as an internal reference. The samples were scanned 100 times.

*Osmometry.* The molecular masses of the telechelics were determined with vapour pressure osmometry (v.p.o.). A range of four solutions was used varying from 5 to 40 g l<sup>-1</sup>. The measurements were carried out at 36.6°C in chloroform. Benzil (1,2-diphenyl-1,2-ethanedione) was used as a reference.

*Titration.* MA end groups were determined by titration with sodium methoxide<sup>19</sup> (1 mol of sodium methoxide will react with 1 mol of anhydride). Thymol blue was used as an indicator.

### MA functionalized PIB

Addition of MA to the PIB telechelic was performed in two ways: one- and two-step methods were used.

*One-step synthesis.* A mixture of PIB-Cl (1.5 g, M<sub>n</sub> = 1300) and MA (0.6 g) was heated to 190°C in the bulk in a nitrogen atmosphere for 12 h<sup>20</sup>. At this temperature, the viscosity of the telechelics was low (< 100 cP) so that magnetic stirrers were used for mixing.

The reaction was performed under a blanket of nitrogen gas. At the end, the reaction mass was cooled and dissolved in hexane. Unreacted MA and the black poly(maleic anhydride) are not soluble in hexane and were removed by filtration. The telechelic PIB was isolated by evaporating the hexane with a rotary evaporator and drying in a vacuum oven for 16 h at 80°C. This final step removed the last traces of unreacted MA.

*Two-step synthesis.* The PIB-Cl was first selectively dehydrochlorinated to PIB-U according to a method described in the literature<sup>21</sup>. The product was then converted to the anhydride terminated product (PIB-MA) in a second step using three different methods.

*Bulk.* Reaction of PIB-U with MA in the bulk was carried out by mixing PIB-U with MA and heating the mixture for 12 h at 190°C. The reaction conditions and work-up were the same as described above.

*Solvent.* For the addition reaction in solution, PIB-U (1.5 g) and MA (0.6 g) were dissolved in benzyl alcohol (25 ml). This mixture was reacted at 190°C for 12 h. The insoluble fraction was then filtered off. The solvent was evaporated with a rotary evaporator and the product was dried in a vacuum oven at 140°C overnight. This also removed the last traces of MA.

*Catalyst.* A reaction vessel was filled with MA (0.6 g) and PIB-U (1.5 g) dissolved in methylene chloride (25 ml). To this mixture was added TiCl<sub>4</sub> (0.2 mol) as a Lewis acid. This mixture was refluxed at 41°C for 16 h. The methylene chloride was evaporated and the reaction products were dissolved in hexane. The catalysts and the unreacted MA could now be filtered off.

The same reaction was performed with AlCl<sub>3</sub>, which also acts as a Lewis acid under these conditions<sup>22</sup>.

### Addition of diaminoethane to PIB-MA

The PIB-MA oligomer was mixed with excess diaminoethane. This was carried out by slowly adding a solution of PIB-MA (15 g) in toluene (80 ml) to a refluxing solution of diaminoethane (2.1 g) in toluene (60 ml). After 2 h at 111°C, the toluene was vacuum evaporated. The oligomer was dissolved in hexane and the unreacted diamine was removed by washing the hexane solution with water and evaporating the hexane layer with a rotary evaporator.

The amic acid that was formed was transformed to an imide by a ring closing reaction at 110°C in a vacuum oven for 24 h.

## RESULTS AND DISCUSSION

### Dehydrochlorination

*I.r. analysis.* PIB absorbs very weakly in the i.r. region. Large amounts of PIB could be used so that strong absorption bands of the end groups could be obtained. The characteristic bands of the PIB main chain and some end groups are given in Table 1. Figure 1 shows the i.r. spectrum before and after dehydrohalogenation.

The absorption of the NaCl support disc masks the absorption of the chlorine end group at 640 cm<sup>-1</sup>. For this reason, the spectrum in Figure 1a was made with a NaCl plate in the reference beam.

The unsaturated end groups of PIB-U absorb strongly

at 890 and 1640  $\text{cm}^{-1}$ . The band at 890  $\text{cm}^{-1}$  is particularly clear, even at low levels of unsaturation. Unsaturated end groups could be traced with i.r. at concentrations that were too small to detect with  $^1\text{H}$  n.m.r.

*N.m.r. analysis.* PIB has a rather simple  $^1\text{H}$  n.m.r. spectrum (Figure 2). The main chain of PIB shows two single peaks at 1.11 and 1.42 ppm. Also present are some small unknown peaks in the 1.0–2.3 ppm range. The end groups and the bulk part of the chain have reasonably different peak positions so that the end groups of the telechelics can be examined and compared with the bulk (Figure 2A). The PIB-Cl shows four separate peaks (a–d). Two of these peaks (a, b) originate from the main chain while the two smaller peaks (c, d) are produced by the end unit (Table 2).

The  $^1\text{H}$  n.m.r. spectrum of PIB-U (Figure 2b) shows the disappearance of the methyl and methylene groups, adjacent to the chlorine (Figure 2A, c, d), and the appearance of new peaks from the unsaturated end group at 4.85, 4.65, 1.78 and 2.00 ppm (Figure 2B, e–h). No peak is visible at 5.15 ppm, as would be the case if there was a 2,3-double bond (endo). From the spectrum it can therefore be concluded that the double bond formed is exclusively a 1,2-bond (exo).

#### MA addition

*I.r. analysis.* For the PIB-MA oligomer, two strong anhydride i.r. bands at 1790 and 1855  $\text{cm}^{-1}$  and a minor

**Table 1** Main i.r. bands of PIB and its end groups with their assignments

	Wavelength ( $\text{cm}^{-1}$ )	Intensity <sup>a</sup>	Origin	
PIB main chain	2980	s	CH stretch	
	2950	s	CH stretch	
	2890	s	CH stretch	
	2720	w	CH stretch	
	1465	s	CH bend	
	1385	s	CH <sub>3</sub> swing	
	1360	s	CH <sub>3</sub> swing	
	1225	s	C—H bend in —CH <sub>2</sub> —	
	1160	m		
	950	m		
	920	m	C—C stretch	
	Chlorine group	640	vw	Cl
	Unsaturated group	3080	m	=CH <sub>2</sub> asym. stretch
1780		w	=CH <sub>2</sub> wag	
1640		m	C=C stretch	
890		s	=CH <sub>2</sub> wag	
Anhydride group	1855	s	C=O sym. stretch	
	1780	vs	C=O asym. stretch	
	715	m		

<sup>a</sup>vs, very strong; s, strong; m, medium; w, weak; vw, very weak

**Table 2.**  $^1\text{H}$  n.m.r. peak positions from Figure 2

H	Chemical shift (ppm)	
a	1.11	Singlet
b	1.42	Singlet
c	1.68	Singlet
d	1.96	Singlet
e	1.78	Singlet
f	1.99	Singlet
g	4.65	Singlet/possibly doublets
h	4.82	Singlet/possible doublets

band at 715  $\text{cm}^{-1}$  were found (Table 1, Figure 1C). Although the anhydride was present only in the end groups, it had an absorbance of the same order of magnitude as the strong bands in the PIB main chain.

The unsaturated band seen at 890  $\text{cm}^{-1}$  in the case of PIB-U, had disappeared completely in the i.r. spectrum of PIB-MA. According to the reaction mechanism, a new double bond was formed but this could not be observed with i.r. It is possible that the band is shifted 30  $\text{cm}^{-1}$  and is obscured behind the adjacent C—C stretching band. That this group is present can be seen in the n.m.r. spectrum.

On the other hand, the absorption of the anhydride asymmetric C=O stretching band at 1790  $\text{cm}^{-1}$  is very strong. For PIB-MA samples with known (titrated) MA concentration, the i.r. transmission ratio was determined by comparing the logarithmic height of the anhydride band at 1790  $\text{cm}^{-1}$  with the logarithmic height of the PIB band at 1390  $\text{cm}^{-1}$  (Figure 3). As the samples had only a low MA content, some high MA concentrations were made by mixing MA with PIB. The i.r. transmissions of these mixtures in tetrahydrofuran (THF) are also presented in Figure 3. Through data derived with both methods, one line can be drawn. The slope of this line can be represented by:

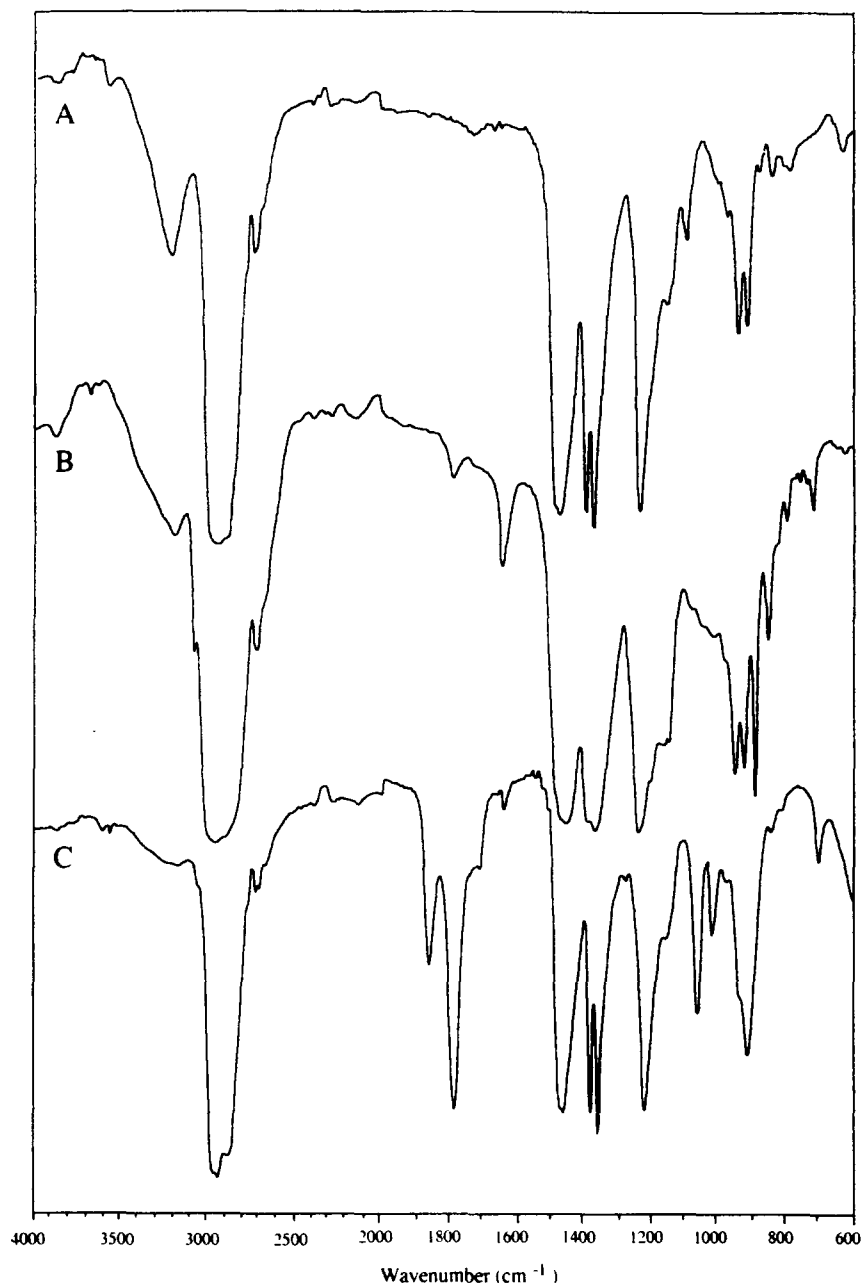
$$\frac{[\text{MA}]}{[\text{IB}]} = 0.024 \times \frac{\text{peak height at } 1785 \text{ cm}^{-1}}{\text{peak height at } 1390 \text{ cm}^{-1}}$$

This relation was used for a rough analysis of the anhydride content of other samples.

*N.m.r. analysis.* The peak assignments of Tessier and Maréchal<sup>16,23,24</sup> were followed. The presence of the anhydride groups is difficult to observe by  $^1\text{H}$  n.m.r., because the two protons give several small peaks distributed over a broad range that lies around 2.5 ppm. (See, for example, the comparable spectra of octadecylsuccinic anhydride or 1-docosenyl succinic anhydride<sup>25</sup>.) Only the newly formed unsaturated group gives one clearly visible peak at 4.91 ppm. The peaks from the original unsaturated bond have disappeared. The n.m.r. spectrum of PIB-Cl and PIB-U compares very well with those of Tessier and Maréchal.

*Conversions of monofunctional PIB.* The addition of MA to PIB was measured by the absorption ratio of two characteristic bands in the i.r. spectrum. The fraction of MA groups can be correlated with the number-average molecular weight ( $M_n$ ) in order to determine the functionality. The data presented in Table 3 were derived from monofunctional oligomers from the same polymer batch, with a  $M_n$  of 1800  $\text{g mol}^{-1}$ . Using one batch eliminates the differences between the results due to errors in the determination of  $M_n$  of these monofunctional oligomers. Reaction of the MA directly with the PIB-Cl at high temperatures (no. 1) gave low MA addition. Synthesis in two separate steps with the bulk method (no. 2) gave a high conversion. A high temperature reaction carried out in benzyl alcohol as solvent (no. 3) gave lower conversions. A low temperature reaction with  $\text{TiCl}_4$  as catalyst in refluxing  $\text{CH}_2\text{Cl}_2$  gave good results (no. 4) but poor results if  $\text{AlCl}_3$  was used as catalyst (no. 5).

The high temperature reaction with the PIB-U is the most effective. This conversion method was therefore used in our further synthesis with difunctional oligomers. The conversion on the whole is low but probably has a



**Figure 1** I.r. spectra of telechelic PIB: (A) chlorine terminated PIB; (B) the same telechelic after dehydrochlorination; (C) telechelic after MA addition

**Table 3** Maleic anhydride addition as a function of reaction conditions. A monofunctional PIB ( $M_n = 1800 \text{ g mol}^{-1}$ ) was used

No.	PIB end groups	Solvent	Catalyst	Temperature (°C)	MA/PIB (i.r. signal ratio) <sup>a</sup>	Functionality
1	PIB-Cl	None	None	190	0.33	0.26
2	PIB-U	None	None	190	1.04	0.83
3	PIB-U	Benzyl alcohol	None	190	0.71	0.57
4	PIB-U	CH <sub>2</sub> Cl <sub>2</sub>	TiCl <sub>4</sub>	42	0.82	0.67
5	PIB-U	CH <sub>2</sub> Cl <sub>2</sub>	AlCl <sub>3</sub>	42	0.17	0.14

<sup>a</sup>Bands at 1785 and 1390 cm<sup>-1</sup>

systematic error caused by a poor molecular weight determination of this particular polymer batch.

**Difunctional PIB.** For the reasons described above, the synthesis of functional PIB-U was performed in the bulk. The data of MA addition to difunctional oligomer are given in *Table 4*. Functionalities above 2 (no. 8 and

no. 9) are very unlikely and are probably due to an inaccuracy of the molecular weight determination. The osmometric data on which the functionality is based had a precision of  $\pm 10\%$ . All oligomers used in our further investigations had a calculated functionality above 90%.

The telechelic PIB-MA was colourless only in some cases. In most cases, the polymer was yellowish to light

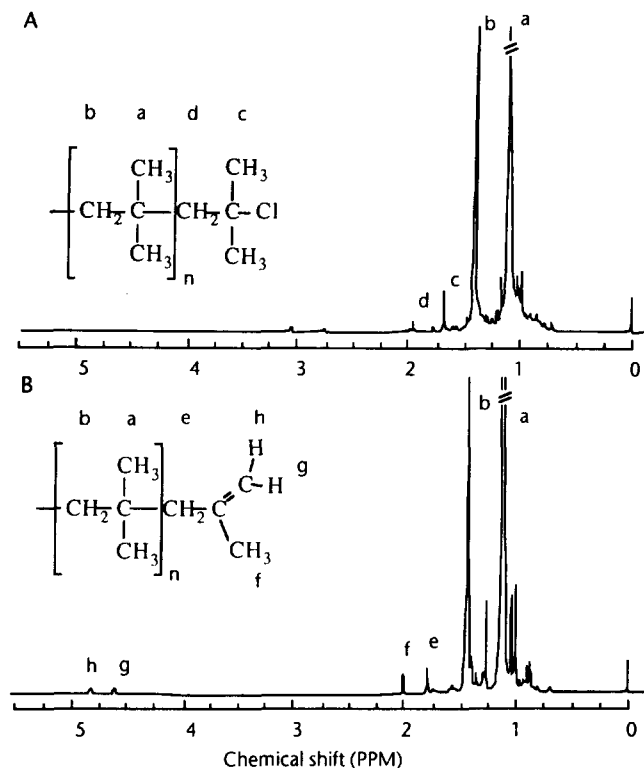


Figure 2  $^1\text{H}$  n.m.r. spectra of a PIB-Cl telechelic (A) and the same telechelic after dehydrochlorination to PIB-U (B)

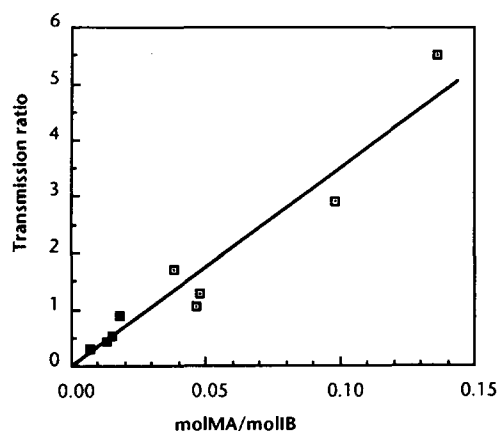


Figure 3 Calibration of PIB/MA transmission of the i.r. bands at 1785 and 1390  $\text{cm}^{-1}$  as a function of the molar ratio: (■) titrated data; (□) mixtures of MA with PIB

Table 4 Maleic anhydride addition at PIB-U

No.	$M_n$ (v.p.o.) ( $\text{g mol}^{-1}$ )	MA ( $\text{mmol g}^{-1}$ )	Functionality <sup>a</sup>
6	2310	0.85	2.0
7	2310	0.80	1.8
8	1930	1.18	2.3
9	1930	1.08	2.1

<sup>a</sup>Data contain an error due to error in  $M_n$

brown. This colouring is thought to originate from poly(maleic anhydride).

#### Diaminoethane addition

The reaction of the PIB-MA with diaminoethane was examined in order to evaluate the possibility of synthesizing

endcapped PIB. The anhydride can react with amine groups with the formation of an amic acid bond that can be converted in a second heating step to a very stable imide bond. I.r. spectroscopy showed the complete disappearance of the anhydride (1800  $\text{cm}^{-1}$ ), and the formation of an amide bond (1550 and 1635  $\text{cm}^{-1}$ ). After the first step, only a small amount of imide (1705  $\text{cm}^{-1}$ ) was found. I.r. spectroscopy showed that the amic acid bond was converted to the imide bond in the second step.

## CONCLUSIONS

Synthesis of anhydride terminated PIB telechelics (PIB-MA) in one step by heating a chlorine terminated PIB in the presence of MA gives only a low conversion. In this bulk process an unsaturation at the  $\beta$ -position (endo) was formed, which reacts slowly in the successive ene reaction.

The synthesis of PIB-MA was carried out in two steps, by first selectively removing HCl to form an  $\alpha$ -unsaturation (exo). Maleic anhydride was, in the second step, successfully added to this double bond as shown by i.r. and n.m.r. Conversion to amine end groups is possible by adding diaminoethane to PIB-MA.

## ACKNOWLEDGEMENT

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