

## New Telechelic Polymers and Sequential Copolymers by Polyfunctional *Initiator-Transfer Agents* (INIFERS)

### 23. Interactions Between Alcohol-Telechelic Linear and Three-Arm Star Polyisobutylenes and Pyromellitic Dianhydride

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#### SUMMARY

Linear and three-arm star hydroxy-telechelic polyisobutylenes have been quantitatively esterified with pyromellitic dianhydride in the presence of 4-N,N'-dimethylaminopyridine in tetrahydrofuran at room temperature. Chain extension occurred only under reflux conditions (67°C). In the presence of chromium acetyl acetonate catalyst at 140°C insoluble networks were obtained within minutes.

#### INTRODUCTION

Linear and three-arm star polyisobutylenes (PIB's) carrying respectively two and three tert-chlorine end groups (tert-chlorine-telechelic PIB's) are useful for the synthesis of a great variety of other telechelic PIB's (1-4). This communication concerns a brief exploration of reactions occurring between linear and three-arm star hydroxy telechelic PIB's and pyromellitic dianhydride (PDA), in particular the esterification and extension of linear PIB diols, and the cross-linking of three-arm star PIB triols with PDA.

#### EXPERIMENTAL

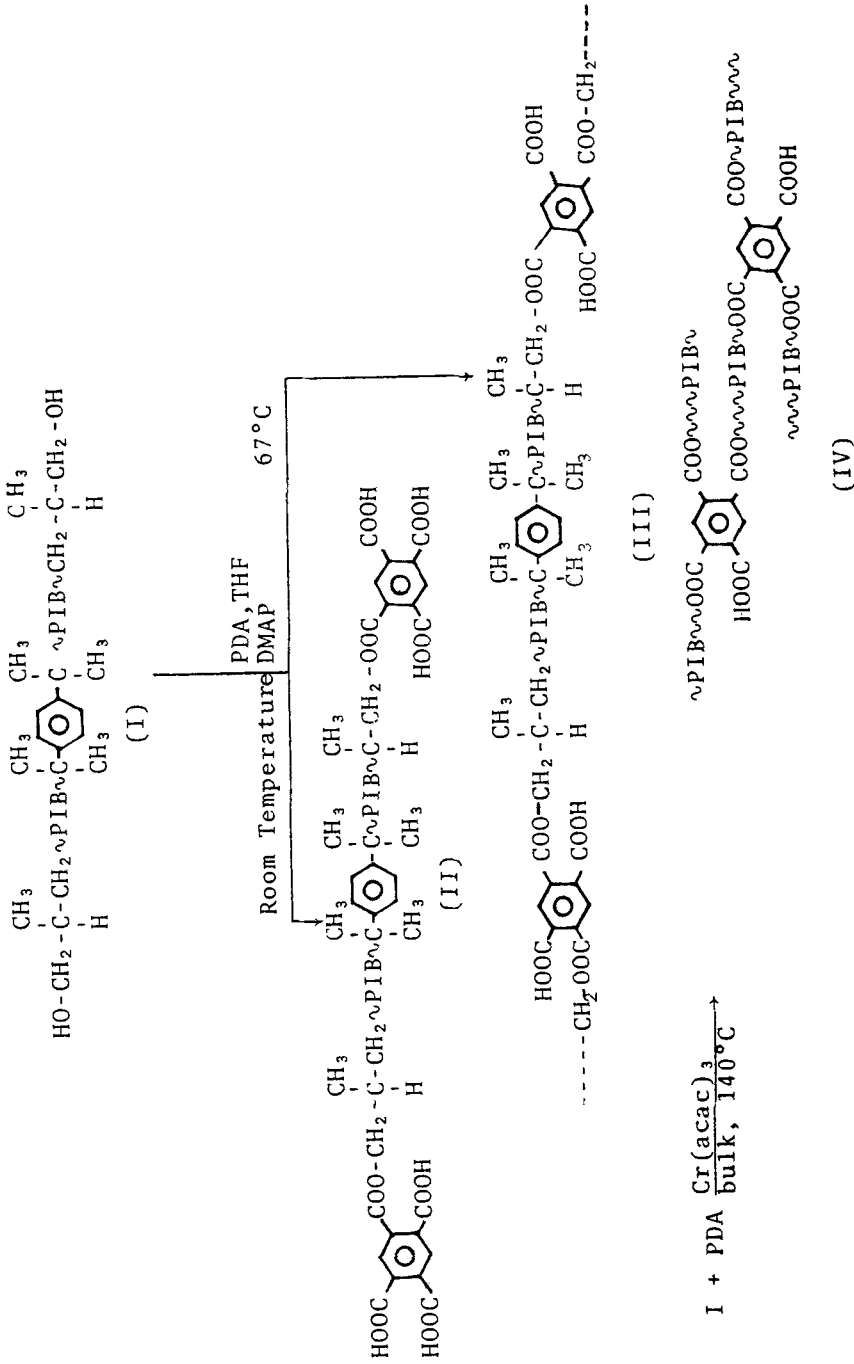
Materials. Pyromellitic dianhydride PDA (Aldrich) was kept at 200°C for 24 hours prior to use. 4-N,N'-dimethylaminopyridine DMAP (Aldrich) and Cr(acetylacetonate)<sub>3</sub> Cr(acac)<sub>3</sub> (Alfa) were used as received. Tetrahydrofuran THF was dried over LiAlH<sub>4</sub>. The synthesis and characterization of  $\alpha,\omega$ -di(hydroxy)PIB ( $\bar{M}_n = 2000$ ,  $\bar{M}_w/\bar{M}_n = 1.7$ ,  $\bar{F}_n = 2.0$ ) and three-arm star OH telechelic PIB ( $\bar{M}_n = 16,500$ ,  $\bar{M}_w/\bar{M}_n = 1.8$ ,  $\bar{F}_n = 3.0$ ) have been described (5-9). In addition, polymer terminal functionalities were also determined by quantitative esterification of -OH end groups with p-cyanobenzoyl chloride in the presence of DMAP followed by <sup>1</sup>H-NMR spectroscopic analysis of the integrated areas associated with the aromatic protons in the p-cyanobenzoyl group relative to the aromatic protons of the inifer residue (10).

Techniques. <sup>1</sup>H-NMR analysis was carried out by using a Varian T-60 NMR spectrometer at room temperature, polymer solutions in CCl<sub>4</sub> and TMS as the internal standard. A Perkin-Elmer 521 infrared spectrophotometer was used to record IR spectra of polymer films on KBr pellets. The molecular weights were determined by GPC as reported (10).

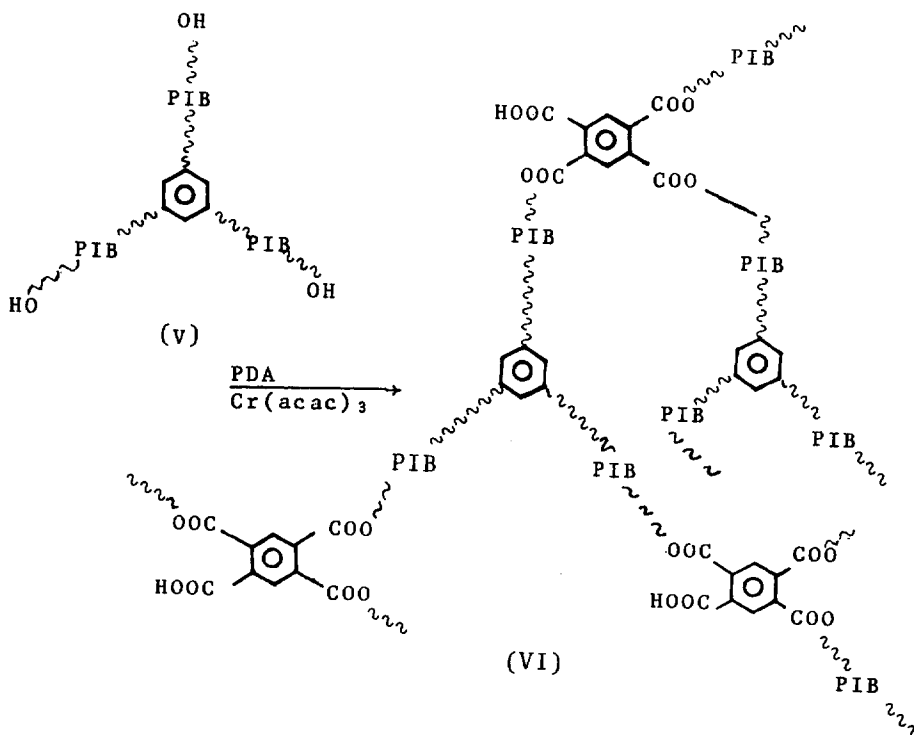
SYNTHETIC PROCEDURES (The roman numerals refer to compounds in Schemes 1 and 2)

Synthesis of II. To 5.6 g (0.0028 mole, 0.0056 mole -OH,  $\bar{M}_n = 2000$ ,

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SCHEME 1: Schematic representation of interactions between  $\alpha, \omega$ -di(hydroxy)-PIB and pyromellitic dianhydride



SCHEME 2: Schematic representation of interactions between three-arm star hydroxy-telechelic polyisobutylene and pyromellitic dianhydride

$\bar{M}_w/\bar{M}_n = 1.7$ ) I dissolved in 50 ml dry THF and stirred under nitrogen at room temperature were added solutions of 1.31 g (0.006 mole) PDA in 20 ml THF and 0.63 g (0.0056 mole) DMAP in 5 ml THF. The course of the reaction was followed by withdrawing samples from time to time and examining their molecular weight and distribution by GPC. The ratio  $(UV)_{\max}/(RI)_{\max}$  was determined as a function of time. While the  $\bar{M}_n$  remained largely unchanged, the  $(UV)_{\max}/(RI)_{\max}$  ratio increased monotonously and reached unity after  $\sim 65$  hours (Figure 1). After 90 hours of reaction the polymer was recovered; it was repeatedly reprecipitated from hexanes into acetone, washed with water and dried. The IR spectrum of the ester shown in Figure 2 exhibits a strong absorption at  $1700\text{ cm}^{-1}$  characteristic of the C=O group.

**Synthesis of III.** To a stirred refluxing solution ( $67^\circ\text{C}$ ) of 5.6 g (0.0028 mole, 0.0056 mole -OH,  $\bar{M}_n = 2000$ ) I in 50 ml THF were added under nitrogen 0.61 g (0.0028 mole) PDA in 20 ml THF and 0.63 g (0.0056 mole) DMAP in 5 ml THF. The molecular weight as a function of time was followed by GPC. The infrared spectrum of the product was similar to that of II.

**Synthesis of IV.** A solution of 2.7 g (0.00135 mole,  $\bar{M}_n = 2000$ ) I, 0.29 g (0.00135 mole) PDA and 0.47 g (0.00135 mole) Cr(acac)<sub>3</sub> in 50 ml dry toluene was heated to  $140^\circ\text{C}$  in a stream of dry nitrogen and the solvent was removed. The reaction was continued in bulk and its progress was followed by withdrawing samples from time to time and analyzing by GPC. After 120 minutes the product became partially insoluble. Figure 3 shows the depend-

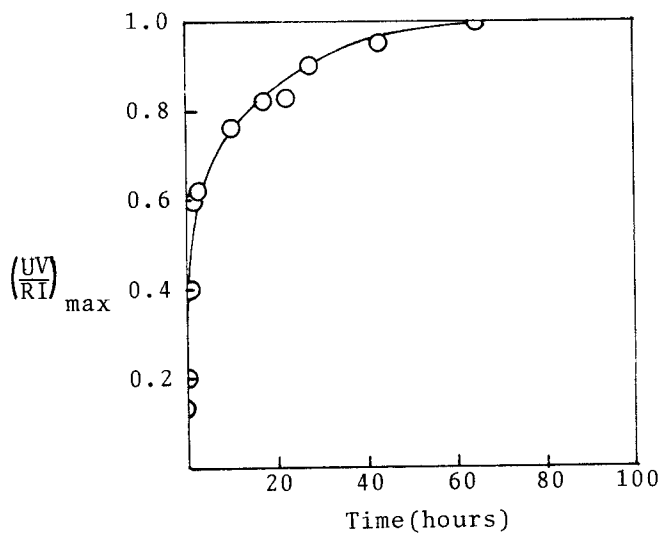


Figure 1. Plot of  $(\frac{UV}{RI})_{max}$  versus time.  
Reaction conditions: room temperature,  
THF, DMAP as catalyst

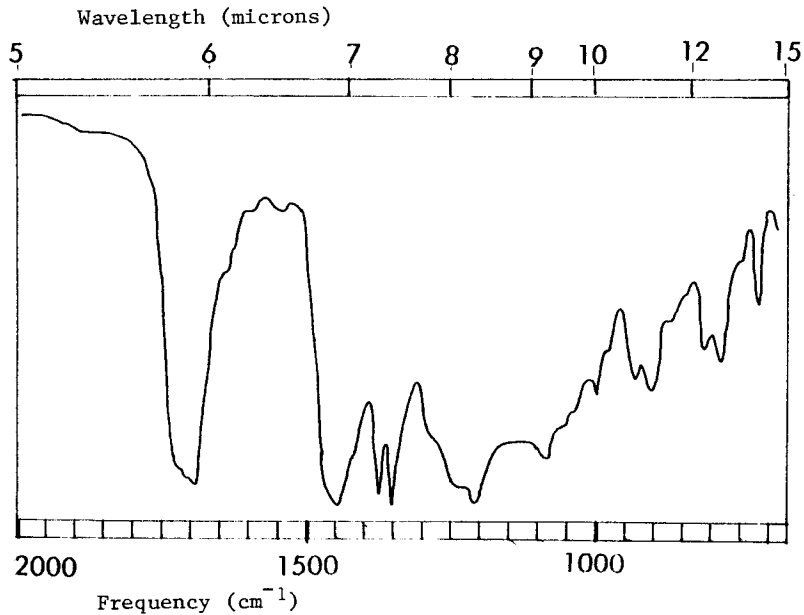


Figure 2. IR Spectrum of  $\alpha,\omega$ -di(carboxylate)polyisobutylene

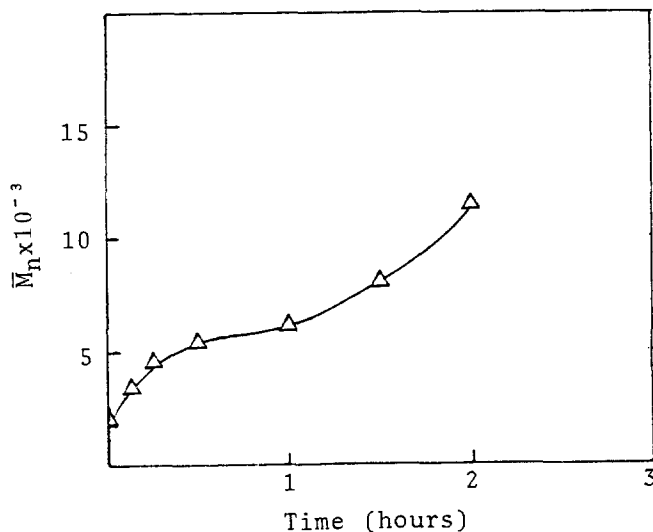


Figure 3. The change in  $\bar{M}_n$  of IV as a function of time ( $\text{Cr}(\text{acac})_3$  at  $140^\circ\text{C}$ )

ence of  $\bar{M}_n$  on reaction time. Even after a few minutes the polymer became insoluble in hexanes. After 15 hours, only 27% of the polymer was soluble in THF ( $\bar{M}_n$  of soluble fraction = 8000).

Synthesis of VI. In 40 ml dry toluene under a blanket of nitrogen were dissolved 1.94 g (0.0001212 mole), 0.000364 mole  $-\text{OH}$ ,  $\bar{M}_n = 16,000$ ,  $\bar{P}_n = 3.0$ ) V, 0.04 g (0.000182 mole) PDA and 0.06 g (0.000182 mole)  $\text{Cr}(\text{acac})_3$ .

The solvent was then evaporated by slowly raising the temperature to  $140^\circ\text{C}$  and the reaction was continued in bulk at this temperature. During the removal of the toluene the charge turned to gel and the progress of the reaction could not be followed by GPC. After 15 hours at  $140^\circ\text{C}$  the insoluble fraction reached 90% of the charge.

#### RESULTS AND DISCUSSION

Schemes 1 and 2 summarize the chemical transformations investigated. One aim of our studies was the preparation of linear  $\text{COOH}$ -telechelic PIB's carrying more than one  $-\text{COOH}$  terminus per chain. We theorized that this goal could be achieved by esterifying hydroxy-telechelic PIB's with stoichiometric quantities of PDA. After considerable preliminary experimentation conditions have been found for quantitative esterification in the presence of DMAP catalyst at room temperature. Figure 1 shows the time profile of the  $(\text{UV})_{\text{max}}/(\text{RI})_{\text{max}}$  ratio (i.e., the maximum of the UV absorption and RI obtained by GPC). The fact that this ratio reaches unity while  $\bar{M}_n$  remains largely unchanged (as determined by GPC) suggests quantitative esterification.

Chain extension occurred by raising the temperature to reflux conditions ( $\sim 67^\circ\text{C}$ ). As shown by the data in Table I, the molecular weights increased at least three fold and the molecular weight dispersity broadened significantly after 40 hours of heating.

TABLE I  
Chain Extension of Hydroxy-Telechelic  
PIB with PDA in the Presence of DMAP

Time hr.	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Extension <sup>a</sup>	
				$\bar{M}_{n_t}/\bar{M}_{n_0}$	$\bar{M}_{w_t}/\bar{M}_{w_0}$
0	2000	3400	1.7	1	1
16	3200	8000	2.5	1.6	2.35
40	6000	16500	2.75	3.0	4.85

<sup>a</sup> $\bar{M}_{n_t}$  and  $\bar{M}_{w_t}$  are number and weight average molecular weights respectively, at time t, and  $\bar{M}_{n_0}$ ,  $\bar{M}_{w_0}$  at time 0

The latter polymer was insoluble in hexanes,  $\text{CCl}_4$  and  $\text{CHCl}_3$  but dissolved in THF. The reaction of hydroxy-telechelic PIB's with PDA at  $140^\circ\text{C}$  was carried out in the presence of  $\text{Cr}(\text{acac})_3$  as esterification catalyst. Thus in the case of the diol I the  $\bar{M}_n$  increased from 2000 to 11,500 within 2 hours (Figure 3). The reaction between the Triol V and PDA could not be followed by GPC because gelation occurred after a few minutes of heating.

#### ACKNOWLEDGEMENT

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