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Polymers from Multifunctional Isocyanates. 9.[†] Alternating Copolymers from 2-Propenyl Isocyanate and Maleic Anhydride

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ABSTRACT: Isopropenyl isocyanate was shown to have electron-donating properties in free radical copolymerization with the electron-deficient monomer maleic anhydride. Alternating copolymers were obtained over a wide range of composition in the monomer feed. The reactivity ratios were found to be 0.01 or less for each mononer. Formation of a charge transfer complex could be proven by NMR spectroscopy. The alternating behavior is also favored by the very low tendency of both monomers to undergo homopolymerization. Analysis of the configuration of building blocks revealed random incorporation of 2-isocyanatopropene, while maleic anhydride was incorporated preferentially in one diastereomeric sequence, which is in agreement with the formation of a charge transfer complex taking part in the propagation reaction. The new poly(2-propenyl isocyanate-*alt*-maleic anhydride) [IUPAC name: poly(tetrahydro-2,5-dioxo-3,4-furandiyl)(1-isocyanato-1-methylethylene))] polymers are glassy and the functional groups are stable toward reaction with each other up to approximately 150 °C.

Introduction

Alkenyl isocyanates with the isocyanate group directly attached to a carbon–carbon double bond (vinyl isocyanate, isopropenyl isocyanate) have been used in free radical polymerization across the double bond and also in anionic polymerization of the heterocumulene system.[2,3] Homopolymers of vinyl isocyanate from either and both polymerizable groups are known though it is difficult to prevent the remaining function from further reaction with the result that upon storage nonmelting cross-linked structures are obtained. The majority of products found in the literature are copolymers which can be cross-linked by step polyaddition with difunctional active hydrogen-bearing nucleophilic compounds. In these copolymers only minor amounts of the isocyanates are required and incorporated.[4–7] In combination with styrene and methyl methacrylate the latter are incorporated preferentially, while with vinyl chloride and methyl acrylate the isocyanates are the main constituents. No regular structures have been described so far.

In the course of our ongoing work with novel polymers based on isocyanate group containing monomers, we learned that the isocyanate moiety is a strong electron-donating substituent if in conjugation with an electron acceptor.[8] This prompted us to look at the electronic properties of the isocyanate group in olefinic systems which we expected to show the same tendency as in aromatic systems. Electronic properties of substituents mainly govern the type of initiation in chain polymerization and the sequence of comonomers in free radical copolymerization of alkenes. Electron-rich monomers are known to form alternating copolymers with electron-deficient monomers.[9]

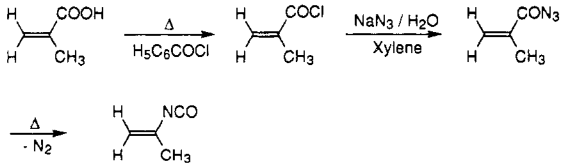
In a previous short communication we reported on a first example of an alternating copolymer from maleic anhydride and vinyl isocyanate to demonstrate the electron-donating nature of the isocyanate group in the copolymerization with a typical electron-deficient monomer.[1] Vinyl isocyanate, however, has the shortcomings of a low boiling point (45 °C), which makes it somewhat difficult to handle the hazardous material, and secondly a high reactivity of both functional groups, which requires stabilization of the monomer. Therefore we chose 2-isocyanatopropene, which boils almost 20 °C higher, for an in-depth investigation of the copolymerization behavior with maleic anhydride, i.e., reactivity ratios, structure of the polymer, etc.

Unlike vinyl isocyanate, isopropenyl isocyanate has almost no tendency to undergo homopolymerization. Because of the methyl group in the isocyanate building block, a tertiary isocyanate group is obtained in the final copolymer, which should enhance the stability toward oxidative degradation and increase the solubility of the polymer as compared to vinyl isocyanate.

In this paper we present the results of the investigation of the copolymerization of maleic anhydride and 2-isocyanatopropene.

Results and Discussion

Synthesis of Monomers and Copolymers. Isopropenyl isocyanate can be synthesized by phosgenation of acetone-based enamines[10,11] and from suitable methacrylic acid derivatives by a rearrangement reaction.[12] The easiest way to obtain it on a laboratory scale is the synthesis via methacryloyl chloride which is transformed into the azide and after thermal decomposition followed by a Curtius rearrangement gives the corresponding isocyanate. The method applied (eq 1) was essentially that reported by Hart.[13]



(1)

Copolymerization of 2-isocyanatopropene with maleic anhydride was made in bulk and in solution (eq 2). The two monomers are miscible under the conditions of bulk polymerization, which gives high yields of polymer and reasonable viscosities. A drawback, however, is the workup of the highly viscous almost gellike reaction mixture, which has to be dissolved in acetone or dimethylformamide first and must be precipitated in an aprotic nonsolvent like

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[†] Part 8: cf. ref 1.

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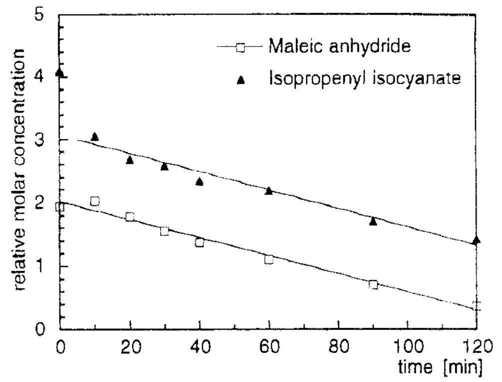


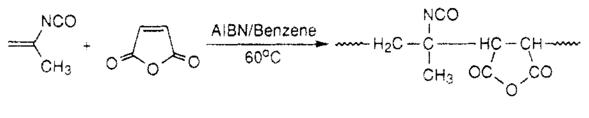
Figure 1. Copolymerization of 2-isocyanatopropene and maleic anhydride; monomer consumption from ^{1}H-NMR.

Table 1. Copolymerization of 2-Isocyanatopropene (1) with Maleic Anhydride (2) to High Conversion

monomer feed 1/2 molar ratio	reacn time (h)	yield[a] (%)	$\eta_{red.}$[b] (dL/g)	polym comp[c] 1/2 molar ratio
1/1	15	92	0.42	1/1
1/2	24	90	0.26	1/1
2/1	24	93	0.43	1/1
1/3	15	90	0.31	1/1.06
3/1	15	81	0.30	1.04/1
1/9	15	89	0.25	1/1.15
9/1	15	93	0.29	1.12/1

[a] Based on theoretical amount of alternating copolymer. [b] Solvent: acetone. [c] Based on elemental analysis.

toluene, in which maleic anhydride tends to stick to the precipitated polymer. A convenient solvent for precipitation polymerization is benzene since both monomers are soluble while the polymer precipitates from the reaction mixture in the course of the reaction. It is almost pure then especially after drying at 70 °C in vacuo. A solvent for monomers and polymer is 2-butanone, which gives high conversion without increasing the polydispersity due to the heterogeneous reaction.



(2)

Preferred reaction conditions were 10% by weight of total monomer content in benzene and 0.5 mol % of AIBN as initiator. Polymerization was made in a broad range of composition of the monomer feed (from 1:9 to 9:1 isocyanate:maleic anhydride). Because of the volatility of 2-propenyl isocyanate, closed vessels, e.g., NMR tubes, were used for polymerizations and the actual ratio in the feed was determined by ^{1}H-NMR as demonstrated in Figure 1. The diagram shows that a nominal ratio of 4:2 is decreased to almost 3:2 because of evaporation of the isocyanate. This was accounted for in further reactions by leaving only little space for the gas phase.

Copolymerization Behavior of 2-Isocyanatopropene with Maleic Anhydride. Two sets of copolymerizations were made in this investigation. In the first set (Table 1) the composition of the feed was varied to the extreme ratios, and polymerization was brought to high conversion to detect compositional heterogeneity as proof for noncompletely alternating incorporation of monomers. In the second series (Table 2) with the same range of monomer feed as for set one, reaction time was kept constant and polymerization stopped at low conversion. This series was used for the determination of reactivity ratios and of relative polymerization rates.

Table 2. Copolymerization of 2-Isocyanatopropene (1) with Maleic Anhydride (2)

2-propenyl isocyanate (1)/ maleic anhydride (2)			
monomer feed[a]	polym comp[a]	conv[b] (%)	$\eta_{red.}$[c] (dL/g)
86.8/13.2	50.7/49.3	9.2	0.44
78.6/21.4	51.1/48.9	9.6	0.37
64.8/35.2	49.9/50.1	10.1	0.30
52.0/48.0	49.5/50.5	5.9	0.24
36.3/63.7	49.3/50.7	2.9	0.21
25.2/74.8	50.5/49.5	2.7	0.16
13.4/86.6	51.7/48.3	2.4	0.08

[a] Mol % from ^{1}H-NMR. [b] Based on total amount of monomers. [c] Solvent: acetone.

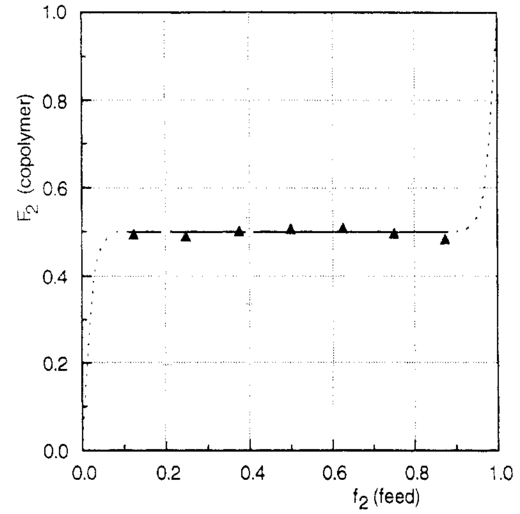


Figure 2. Copolymerization diagram of the monomer pair 2-isocyanatopropene/maleic anhydride.

Conversion of monomers was monitored by ^{1}H-NMR in benzene-d_6 using benzene-d_5 as reference. ^{1}H-NMR is the method of choice since the absorptions of the two monomers do not interfere. Figure 1 clearly demonstrates that equimolar amounts of both monomers are incorporated into the polymer up to 50% total conversion of monomers (80% of theoretical amount of alternating copolymer). The slight increase in maleic anhydride concentration from the initial measurement at room temperature to the first measurement at reaction temperature is probably due to evaporation of solvent.

Copolymerization of 2-isocyanatopropene with maleic anhydride to high conversion required reaction times between 15 and 24 h. In agreement with the results on free radical homopolymerization of both monomers, conversion beyond the amount of alternating copolymer was not observed (Table 1). No indications of compositional heterogeneity were found from NMR spectroscopy and elemental analysis except for the extreme monomer ratios where microanalyses are in agreement with a slightly preferential incorporation of the monomer being in excess in the feed (cf. Table 1).

In the series of copolymerizations made to obtain the reactivity ratios, the initial composition of the monomer feed again was taken from the more precise NMR results. Polymerizations were stopped after 15 min with conversions between 2 and 10% which allows use of the initial concentrations for the determination of the reactivity ratios. Polymer composition was taken from NMR. A copolymerization diagram based on these results is shown in Figure 2 indicating that even at rather high and low ratios in the feed incorporation of equimolar amounts is observed.

Table 3. Reactivity Ratios for 2-Isocyanatopropene/Maleic Anhydride

method	2-isocyanatopropene r_1	maleic anhydride r_2
Kuo–Chen	0.01	0.01
Mayo–Lewis	0.009	0.01
Kelen–Tüdös	−0.018	0.01

Table 4. *Q–e* Values of Isopropenyl Isocyanate (1) and Maleic Anhydride (2)

maleic anhydride lit. data	2-isocyanatopropene	
	calcd from expt.	calcd from lit. data
$e_2 = +3.69$, $Q_2 = 0.86$[19]	$e_1 = +0.65$, $Q_1 = 0$	$e_1 = -1.05$, $Q = 0.16$[19]
$e_2 = +2.25$, $Q_2 = 0.23$[20]	$e_1 = -0.78$, $Q_1 = 0$	$e_1 = -0.80$, $Q = 0.14$[20]

For evaluation of reactivity ratios the procedures according to Mayo and Lewis,[14] Kuo and Chen,[15] and Kelen and Tüdös[16] were used. The reactivity ratios thus obtained vary according to the method applied. This shows the difficulties connected with the experimental determination of reactivity ratios from alternating copolymerizations. The rather small *r* values have big relative error margins so that even negative values were obtained. It seems therefore reasonable to take 0.01 for both r_1 and r_2 (Table 3).

Q–e values according to Alfrey and Price[17] were calculated according to eqs 3 and 4

$$e_1 = e_2(-\ln r_1 r_2)^{1/2} \tag{3}$$

$$Q_1 = Q_2 \exp[-e_2(e_2 - e_1)] \tag{4}$$

from the experimental reactivity ratios for 2-isocyanatopropene (monomer 1) while literature data were used for maleic anhydride[18,19] (monomer 2). Depending on these different *Q–e* values for maleic anhydride, a positive or a negative *e* of about 0.7 is obtained while *Q* is zero in both cases (Table 4). Based on data from a more random type of copolymerization,[19] a negative *e* value is obtained, indicating that 2-isocyanatopropene is of the electron-donor-type.

Monomer consumption after 15 min was used as a measure of relative reaction rates as a function of monomer composition in the feed. Along with the reduced viscosities of the alternating copolymers, these are shown in Figure 3. The rate of polymerization has a maximum for 40% maleic anhydride followed by a decrease at higher anhydride content. Such a behavior has been observed for other monomer/maleic anhydride combinations. It has been explained by formation of charge transfer complexes from the monomers, the concentration of which depends on the relative amounts of the two monomers with a maximum at or close to equimolar amounts of the monomers. These monomer complexes are thought to play a key role in the propagation step of the alternating copolymerization,[20] and in particular a series of 1:1 complexes of maleic anhydride with donor monomers have been investigated.[9,21] Complex constants have been obtained from UV and NMR spectroscopy.[22]

We have not been able to prove the existence of charge transfer interactions by UV spectroscopic investigation of mixtures of the two monomers. A shift of the resonance signals of the protons in maleic anhydride, however, was observed in the NMR spectra in the presence of excess 2-isocyanatopropene. For these measurements Benesi–Hildebrand conditions were ensured; i.e., the electron donor was used in 20–60-fold excess with regard to the acceptor.[23] The Hanna–Ashbaugh relation[24] (eq 5) was used for data treatment.

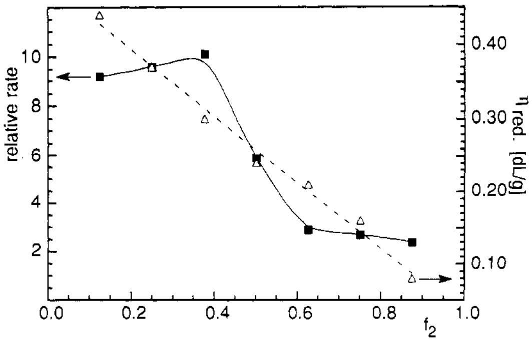


Figure 3. Dependence of the rate of copolymerization and viscosity of copolymers 3 on composition of monomer feed.

Table 5. Chemical Shift Values from NMR Analysis of Maleic Anhydride/2-Propenyl Isocyanate Charge Transfer Complexes, Measured in Cyclohexane

maleic anhydride (mol/L)	isopropenyl isocyanate (mol/L)	δ_{obs} (Hz)	Δ_{obs} (Hz)
0.025	0.000	2682.41	0.00
0.025	0.456	2690.19	7.78
0.025	0.521	2691.82	9.41
0.025	0.931	2697.55	15.14
0.025	1.277	2701.23	18.82
0.025	1.541	2703.13	20.72

$$\frac{1}{\Delta_{obs}} = \frac{1}{K\Delta_{CTC}}\frac{1}{[D]_0} + \frac{1}{\Delta_{CTC}} \tag{5}$$

$$\Delta_{obs} = \delta_{obs} - \delta_f$$

Based on the concentrations of monomers and the NMR data given in Table 5, the reciprocal of the change in chemical shift $1/\Delta_{obs}$ was plotted over the reciprocal of the concentration of 2-propenyl isocyanate $1/[D]_0$ (donor monomer). The data points of Figure 4 were fitted by a linear equation which allows calculation of *K* from the slope and the intercept. A value of 0.37 L/mol for the complex formation constant thus has been obtained.

These results strongly suggest that a charge transfer complex is involved in the copolymerization of 2-isocyanatopropene and maleic anhydride.

Characterization of Poly(2-isocyanatopropene-*alt*-maleic anhydride). The structure of the polymers was proven by infrared and NMR spectroscopy as well as elemental analysis. The infrared spectrum (Figure 5) shows the characteristic absorptions of the isocyanate group at 2280 cm^{-1} and the carbonyl absorptions of the anhydride group at 1840 and 1780 cm^{-1}. No bands are to be seen that could be assigned to products of a reaction of the functional groups.

The ^{1}H-NMR spectrum (Figure 6) proves the alternating structure of the copolymers. Two signals are observed for each group of protons, with the methine protons of the anhydride moiety being the most downfield (3.67/3.82) followed by the methylene protons of the isocyanate building block (2.45/2.48/2.59/2.70/2.86/2.94) and the methyl protons of the latter as the most shielded at 1.81/1.91 ppm.

Isopropenyl isocyanate and maleic anhydride are prochiral molecules which form three chiral centers upon polymerization with different possibilities of diastereomers (Scheme 1). Models for the anhydride unit are 2,3-dialkylsuccinic anhydrides, the ^{1}H- and ^{13}C-NMR spectra

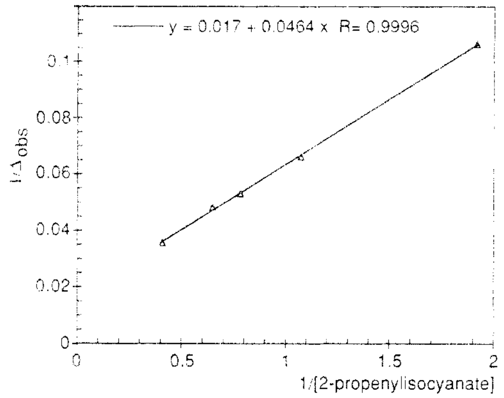


Figure 4. Plot of $1/\Delta_{obs}$ vs concentration of 2-isocyanatopropene $[D]_0$ for determination of complex constant according to eq 5.

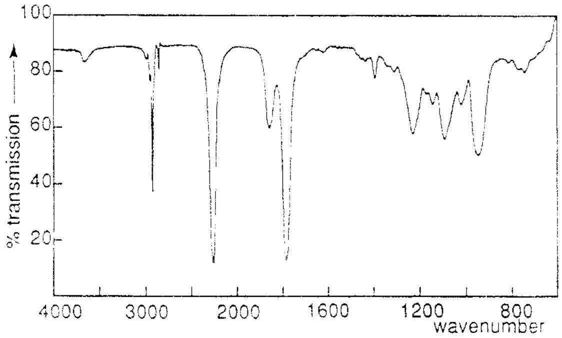


Figure 5. IR spectrum of the alternating copolymer 3.

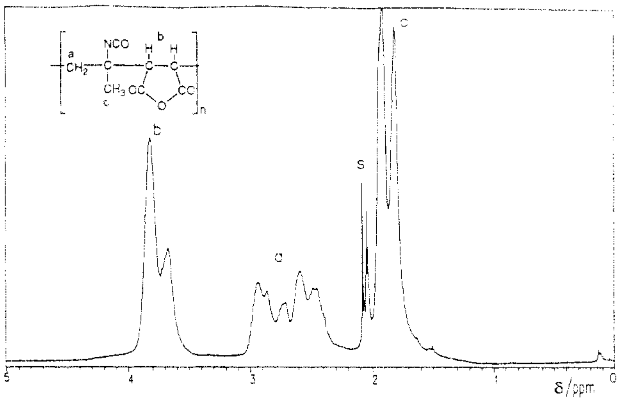
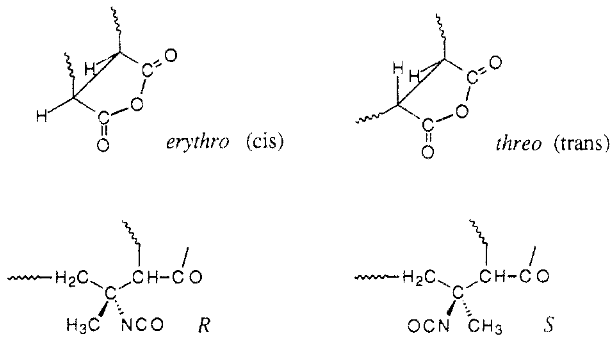


Figure 6. ¹H-NMR spectrum of the alternating copolymer 3.

Scheme 1



of which show characteristic signals for the different diastereomers.[25]

The CH protons of 2,3-diethylsuccinic anhydride have a chemical shift of 3.1 ppm for the *erythro* (*cis*) diastereomer and 2.8 ppm for the *threo* (*trans*) form.[25] The ^{13}C-NMR spectra of the two diastereomers have different chemical shifts for the sp^3 carbons while those of the carbonyl carbons are identical.[26] Both have been used for the analysis of alternating copolymers from maleic anhydride; effects due to different chain conformation, however, were not taken into account.[27] Based on this analysis, the absorptions of the CH protons (3.68 and 3.82 ppm) can be assigned to the *erythro* and *threo* form, respectively, with a preference for the erythro form in a ratio of 5:2. Similar results have been reported with poly(ethylene-*alt*-maleic anhydride).[26] These results can be understood most easily if a charge transfer complex between the two monomers is involved in the propagation step. Otherwise one would expect the trans structure to be favored.

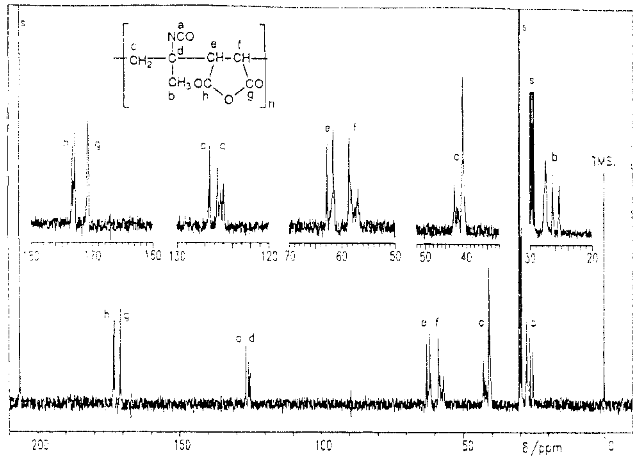


Figure 7. ^{13}C-NMR spectrum of the alternating copolymer 3.

The signals of the methyl protons at 1.91 and 1.81 ppm are probably caused by the two diastereomeric diads. The ratio of the integrals (1:1 within experimental error) implies that there is no preference for either configuration. The resonances of the methylene protons cannot be assigned by simple analogy to known copolymers of similar structure.

The ^{13}C-NMR spectrum of **3** is shown in Figure 7. The methine carbons (C_e and C_f) have two peaks each at 62 and 59 ppm; those at 59 ppm have been assigned to the *erythro* configuration.[26] The other carbon atoms can be identified according to their chemical shift; further analysis requires additional model compounds and computer simulation.

Polymer **3** is a colorless amorphous powder which softens on a heated plate at about 100 °C. From the DSC trace in Figure 8, a glass transition at about 100 °C is observed in the cooling mode. Polymers **3** are stable in the absence of humidity but react quickly with humid air as could be seen from acetone films cast for IR spectroscopy. The films became turbid within minutes when exposed to air. One would expect the two different functional groups to react with each other to give imide structures. No such reaction occurs up to more than 150 °C as shown in the thermal analysis in a dynamic run (Figure 8). When the polymer is heated further to 300 °C, a broad exotherm appears in the DSC above 200 °C. It is accompanied by weight loss as detected by thermogravimetry, which is shown in Figure 9. This is very likely due to formation of imide structures by reaction of the isocyanate with the anhydride.

First results obtained in the investigation of the reactivity of the two reactive groups in the copolymer show that the isocyanate reacts selectively with amines and alcohols under appropriate conditions. The anhydride moiety can react in a second step with the same compounds. This will be the subject of a forthcoming publication.

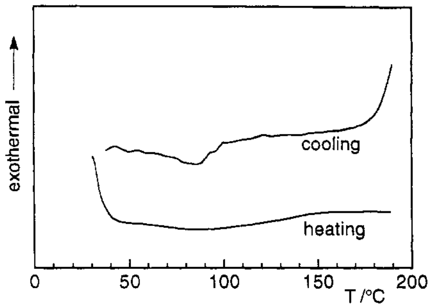


Figure 8. DSC trace of the alternating copolymer **3** (heating rate 20 K/min).

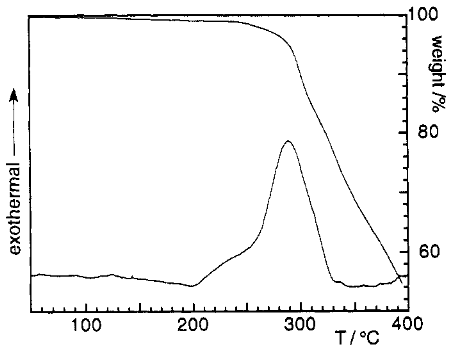


Figure 9. DSC and thermogravimetry of **3**. The weight loss and exotherm are due to imidization.

Conclusions

Based on kinetic and spectroscopic evidence, the isocyanate group has been identified as a potentially electron-releasing substituent in the presence of a strong electron-accepting substituent. Similar electronic behavior was postulated for free radical copolymerization and proven by the first synthesis of an alternating copolymer of 2-isocyanatopropene with maleic anhydride.

As in many other examples of free radical alternating copolymerization, the presence of a donor acceptor complex formed by the two monomers could be proven. This complex can account for the results obtained in terms of rate of polymerization as a function of monomer ratio in the feed and also for the microstructure of the polymer, i.e., preferential *cis* incorporation of the anhydride moiety.

This new class of highly functional and highly reactive polymers with a regular sequence of functional groups opens a wide range of synthetic possibilities to tailor properties of new polymers by selective reaction of the functional groups. We are currently investigating the scope of the reaction in terms of the structure of alkenyl isocyanates and acceptor monomers as well as the possible polymer-analogous reactions.

Experimental Section

Methods of Characterization. IR spectra were recorded on a Bruker IFS 48 FTIR spectrometer. ^{1}H NMR spectra (Bruker WP 80, Bruker AMX-400) and ^{13}C-NMR spectra (Bruker AMX-400) were obtained in deuteriochloroform, acetone-d_6, or benzene-d_6 with tetramethylsilane (TMS) or $CHCl_3$ as internal standard. NMR spectra for the determination of the charge transfer constant were recorded on a Bruker AMX-400 spectrometer. The solvent was cyclohexane containing 10% deuterated cyclohexane. For concentrations of monomers, see Table 5. Viscometry was performed with an Ubbelohde type viscometer. Thermal properties were determined on a Mettler TA 4000 system with DSC 30 and TG 50 equipment.

Materials. Methacrylic acid, maleic anhydride, benzoyl chloride, and sodium azide were purchased from Aldrich. Maleic anhydride was freshly distilled in a Kugelrohr apparatus (Büchi) prior to use. Solvents used were dried according to literature procedures. All reactions were conducted in flame-dried glass equipment in an atmosphere of dry argon.

Methacryloyl Chloride. A 500 mL round bottom flask equipped with a dropping funnel and distillation setup was filled with 86 g (1 mol) of methacrylic acid and 0.5 g of hydroquinone, and 281 g (2 mol) of benzoyl chloride was added. The dropping funnel was replaced by a stopcock, the mixture were heated to 150–160 °C, and the acid chloride distilled off. The crude product was purified by redistillation. Yield: 60%. Bp_{760}: 95 °C. IR: 1750 (CO), 1620 cm^{-1} (C=C). ^{1}H-NMR: ($CDCl_3$/TMS) 2.00 (s, 3H), 6.03 (s, 1H), 6.49 ppm (s, 1H). ^{13}C-NMR: ($CDCl_3$/TMS) 18.33 (s, CH_3), 133.35 (s, CH_2), 140.53 (s, H_2C=C), 166.57 ppm (s, COCl).

2-Propenyl Isocyanate (1). In a 500 mL three-neck flask equipped with a thermometer, dropping funnel, and stirrer 19.5 g (0.3 mol) of sodium azide was dissolved in 70 mL of water cooled to −10 °C. A total of 21 g (0.2 mol) of methacryloyl chloride dissolved in 70 mL of xylene was slowly added. The mixture was stirred at 0 °C for 1 h, and the organic layer was separated, washed once with concentrated sodium carbonate and twice with ice water, and dried over sodium sulfate.

Decomposition of the azide was done in a 250 mL two-neck flask equipped with a dropping funnel and a distillation setup. The flask was filled with 10 mL of xylene, immersed in an oil bath, and heated to 80 °C, and the solution of the azide was added at such a rate that the isocyanate formed distilled off continuously. The crude isocyanate was purified by redistillation. Yield: 69%. Bp_{760}: 64 °C. IR: 2270 (NCO), 1640 cm^{-1} (C=C). ^{1}H-NMR: ($CDCl_3$/TMS) 1.98 (s, 3H), 4.58 (s, 1H), 4.71 ppm (s, 1H); (benzene-d_6) 1.44 (s, 3H), 4.22 (s, 1H), 4.50 ppm (s, 1H). ^{13}C-NMR: ($CDCl_3$/TMS) 23.38 (s, CH_3), 106.41 (s, CH_2), 124.15 (s, NCO), 134.62 ppm (s, CH_2=C).

Poly(2-isocyanatopropene-*alt*-maleic anhydride) (3). In a 50 mL flame-dried flask under nitrogen 0.83 g (10 mmol) of 2-isocyanatopropene and 0.98 g (10 mmol) of maleic anhydride (for a 1:1 ratio) were dissolved in benzene to give a 10% (w/w) concentration, and 16.5 mg of AIBN was added. The mixture was degassed in two freeze–pump–thaw cycles, closed, and polymerized in an oil bath thermostated at 60 °C. Polymerization was stopped by cooling to −20 °C. The polymer was isolated by filtration under argon, washed several times with benzene, and dried at 70 °C in vacuo. IR: 2270 (NCO), 1850 and 1780 cm^{-1} (CO). ^{1}H-NMR: (acetone-d_6, 400 MHz) 1.81/1.91 (3H), 2.45/2.48/2.59/2.70/2.86/2.94 (2H), 3.67/3.82 ppm (2H). ^{13}C-NMR: (acetone-d_6, 100 MHz) 25.2/26.3/27.4 (CH_3), 40.8/42.9 (CH_2), 56.8/58.6 (CH), 61.6/62.7/62.8 (CH), 125.0/125.3/125.6 (quart., C), 126.4 (NCO), 170.7 (CO), 172.8/173.2 ppm (CO). DSC: 320, >400 °C (exotherm). TG onset: 263 °C.

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