Synthesis and Characterization of Glycidyl Azide Polymers Using Isotactic and Chiral Poly(epichlorohydrin)s

Sylvie Brochu and Guy Ampleman*

Energetic Materials Section, Chemistry/Environment Group, Defence Research Establishment, Valcartier, 2459 Pie XI Blvd., North, P.O. Box 8800, Courcelette, Québec, Canada G0A 1R0

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ABSTRACT: Isotactic and chiral glycidyl azide polymers (GAPs) have been synthesized by the reaction of isotactic and chiral poly(epichlorohydrin)s (PECHs) with sodium azide in dimethylformamide at 95 °C. The azidation does not affect the isotacticity of the chains, but the polymer backbone is degraded in the process; a GAP of high molecular weight (100 kg/mol) is nevertheless obtained. Despite the high isotacticity of the polymer chains, the GAPs are not crystalline. Long reaction times favor the branching and/or the cross-linking of the polymer. The isotactic and chiral PECHs used as starting materials for the GAP syntheses have been prepared by the Vandenberg process using racemic or chiral monomers, leading thus to partially ((*RS*)-PECH) or completely ((*R*)- or (*S*)-PECH) isotactic polymers, respectively. They have been split into a soluble and an insoluble fraction by acetone extraction. The fractionation of chiral PECH withdraws from the polymer the incompletely isotactic chains coming from the presence of monomers of opposite configuration in the chiral epichlorohydrin or from a defective polymerization process. The population of crystals remaining in the insoluble chiral PECH fraction is thus more homogeneous, leading to an improved crystallinity and a higher melting temperature.

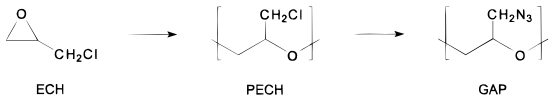
Introduction

High-energy solid compositions, such as propellants, plastic-bonded explosives, or the like, are comprised of an elastomeric binder in which are dispersed particulate solids such as oxidizers, particulate fuel material, or crystalline explosives. Glycidyl azide polymers (GAPs) are being studied as possible energetic binders and for this, they are reacted with a curing agent to form a chemically cross-linked matrix for ammonium nitrate in new insensitive reduced-smoke rocket propellant formulations, and for RDX in new insensitive plastic-bonded explosives. The next generation of propellants and composite explosives will use an energetic thermoplastic elastomer (ETPE) as the binder.

Thermoplastic elastomers (TPE) are copolymers of the type ABA or AB, where A and B are respectively the hard segment and the soft segment. The hard segment is capable of crystallization or association and gives the thermoplastic behavior to the copolymer, whereas B is the soft segment giving the elastomeric behavior to the copolymer. In practice, at room temperature, a thermoplastic elastomer behaves like a rubber because it is cross-linked in the same fashion as a conventional elastomer, but with reversible physical cross-links. Since the physical cross-links are reversible, the TPE can be melted or dissolved in a solvent, mixed with other components of the formulation and processed. A gun or rocket propellant or a composite explosive could be isolated upon cooling or evaporating the solvent. Cooling or evaporating the solvent lets the broken physical cross-links re-form and the elastomeric properties are recovered, leading to an easier process without missed batches. On the other hand, obsolete material can be melted or dissolved before the separation of the components, leading to a recyclable material.

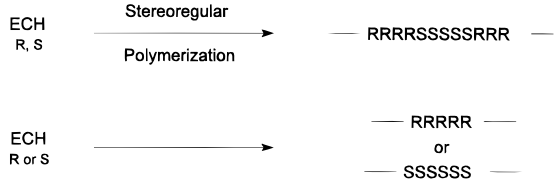
Energetic thermoplastic homopolymers to serve as the hard segment in a TPE are much sought after. It was thought that an isotactic GAP would crystallize, giving the hard segment in a TPE, and could be incorporated in such a copolymer. Even the isotactic GAP itself, containing amorphous and asymmetric sequences of the enantiomers, is by definition a thermoplastic elastomer. For these reasons, the syntheses of isotactic and asymmetric GAPs were studied.

The synthesis of GAP is not accomplished from the polymerization of 1-(azidomethyl)oxirane, because no method of synthesis of this monomer has been found to date. GAP is rather obtained from the polymerization of epichlorohydrin (1-(chloromethyl)oxirane, ECH), followed by the azidation of the resulting poly(epichlorohydrin) (PECH):



(1)

PECH can be obtained either as an atactic polymer, in which the pendant chloromethyl groups are randomly distributed on each side of the chain, or as an isotactic polymer, a more regular structure in which all the lateral groups are located on the same side of the chain. The isotactic polymer can be obtained either by the stereoselective polymerization of the racemic monomer or by the polymerization of the pure enantiomer. In the first case, the polymer chains are constituted of blocks of *R* and *S* units of variable length, with occasional inversions of configuration along the chain. In the second case, all units in the chains are of identical configuration, leading thus to an optically active polymer:



The physical properties of PECH depend on the microstructure of the polymer: atactic PECH is essentially amorphous and has a glass transition temperature of

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−20 to −25 °C, and isotactic PECH is semicrystalline and has a melting temperature of approximately 125 °C. The microstructure of PECH is controlled by the polymerization conditions, and especially by the type of initiator employed: cationic or organometallic initiators are generally used. Cationic initiators such as Lewis acids or tertiary oxonium salts, often complexed with water, alcohol, or ether, lead to an atactic low molecular weight polymer (<4000 g/mol) with hydroxyl end groups.[1,2] Telechelic polymers of molecular weight up to 15 000 g/mol can also be obtained with the use of 1,4-butanediyl ditriflate as the initiator.[3] However, most of the industrial elastomeric PECH is produced by the Vandenberg process[4] using organometallic initiators, which yields a polymer of high molecular weight that is often fractionated into its atactic and isotactic components; the degree of isotacticity of PECH is generally determined by ^{13}C nuclear magnetic resonance spectroscopy.[5,6]

PECH has already been used as a precursor of some liquid crystalline polymers[7−9] and various other polymers.[10−15] Chemical modification of PECH occurs mainly as a nucleophilic substitution reaction at the chloromethyl pendant group, leaving untouched the asymmetric carbon atoms of the polymer backbone; the tacticity of the resulting polymer therefore should not be altered. Several authors have reported however that cleavage of the backbone polymer chain[11,12,14,16−19] and cross-linking[10,11,14,17,18] are important side reactions.

The first synthesis of GAP was reported by Vandenberg in 1972.[20] Amorphous or crystalline poly(epichlorohydrin) of molecular weights greater than 25 000 g/mol was used as the starting material. In 1983, Frankel[21,22] prepared a linear atactic GAP with secondary hydroxyl end groups having a molecular weight ranging from 1000 to 3000 g/mol. It is also possible to obtain azide-terminated low molecular weight GAP using a two-step synthesis developed by Ampleman,[23] which uses a PECH with tosylate end groups as intermediary in the azidation process. Ampleman also shown that PECH and GAP functionality (number of hydroxyl groups per polymer chains) can be increased up to 4 times with a regiospecific epoxidation of low molecular weight linear PECH.[24] Finally, high molecular weight branched GAP has been synthesized by Ahad[17,18] using commercial rubbery PECH as starting material.

To our knowledge, the synthesis and complete characterization of isotactic or chiral GAP of high molecular weight have never been reported. The preparation of such GAPs would however be interesting to see, for example, if their highly regular microstructure can induce the crystallization of the chains, as for isotactic PECHs.[4] The aim of this work is therefore to synthesize high molecular weight GAPs of various isotacticities to determine the influence of the polymer microstructure on its crystallinity. Isotactic and chiral (*R*)- and (*S*)-GAPs are synthesized by the azidation of the corresponding PECHs, obtained by the Vandenberg process;[4] extraction of this material with acetone further broadens the range of isotacticity and molecular weight available for the above-mentioned investigation. The azidation is performed on selected samples of isotactic (*R*)- and (*S*)-PECH. Nuclear magnetic resonance spectroscopy is used to calculate the degree of substitution and the isotacticity of the polymer. The measurement of the polymer molecular weight before and after the azidation is necessary to determine the extent of degradation of the polymer backbone and of cross-linking; viscosimetry is used for PECH and size-exclusion chromatography for GAP. The melting temperatures and enthalpy of fusion of the polymers are evaluated by differential scanning calorimetry.

Experimental Section

Materials. All chemicals were obtained from Aldrich Chemical Co. and used without further purification, unless otherwise stated. Diethyl ether was dried by refluxing one night over calcium hydride, purified by distillation, and kept over sodium wires under a nitrogen atmosphere. Racemic epichlorohydrin was purified by distillation and kept over molecular sieves. (*R*)- and (*S*)-epichlorohydrins were used as received; optical rotation measurements confirmed the enantiomeric excess of 97% given by the supplier.

Polymer Synthesis. The preparation of the $AlEt_3/H_2O$ (1/0.6) catalyst and the polymerization of epichlorohydrin (ECH) are based on the synthesis of Vandenberg.[4] Prior to use, all glassware was flame dried while being flushed with nitrogen, and transfers of liquids were carried out either by cannulation or with a syringe under a nitrogen atmosphere.

Catalyst Preparation. *Caution!* $AlEt_3$ is a pyrophoric and moisture-sensitive material that should be handled with care, always in an inert atmosphere. Anhydrous diethyl ether (210 mL) was transferred in a three-neck round-bottom flask equipped with a condenser, a nitrogen inlet, a magnetic stirrer, and a septum. To determine the precise amount of catalyst in solution, $AlEt_3$ was first transferred by cannulation into a purged graduated storage vessel; then 26.8 g (0.235 mol) was slowly transferred by cannulation into the ether solution, maintaining a gentle reflux. Distilled water (2.54 mL, 0.141 mol) was then added dropwise at a rate slow enough to maintain a gentle reflux. At the end of the addition (about 40 min), the solution was heated under reflux for an additional 2 h period and then allowed to cool to room temperature. The catalyst solution was transferred to a purged distilling flask and always kept under a positive pressure of nitrogen at 5 °C.

Polymerization of Racemic Epichlorohydrin. Anhydrous diethyl ether (400 mL) was transferred in a three-neck round-bottom flask equipped with a dropping funnel, a nitrogen inlet, a magnetic stirrer, and a septum. Freshly distilled epichlorohydrin (107 g, 1.16 mol) was added to the ether solution, and the catalyst solution (40 mL) was transferred to the dropping funnel. The catalyst was added dropwise to the monomer solution over a 90 min period. After 24 h, the polymerization was quenched by the addition of methanol (400 mL). The poly(epichlorohydrin) (PECH) was stirred for 1 h, isolated by filtration, and dried overnight under vacuum at 40 °C (102 g, 95% yield). The catalyst residues were removed by stirring with acetylacetone (AcAc) (7.5 mL/g of PECH) at room temperature for 24 h.[25] Methanol (7.5 mL/mL of AcAc) was added, and the polymer was isolated by filtration and dried overnight under vacuum at 40 °C. More than 95% of the initial polymer was recovered. This PECH was then treated with 4,4′-thiobis(6-*tert*-butyl-*m*-cresol) (Santonox, ICN Biochemicals Canada), which acts as an antioxidant. A typical procedure[4] consists of stirring PECH (10 g) with 100 mL of methanol containing 200 mg of Santonox for 90 min. The polymer was recovered by filtration and dried overnight under vacuum at 40 °C.

Polymerization of (*R*)- and (*S*)-Epichlorohydrin. The procedure is the same as the one of racemic ECH, except that the chiral monomers were used as received; no additional purification was needed. The yields of (*R*)- and (*S*)-poly(epichlorohydrin) ((*R*)- and (*S*)-PECH) were respectively 80 and 78%.

Polymer Fractionation. PECH was extracted 24 h with boiling acetone, using a Soxhlet extractor. The apparatus was insulated with aluminum foil to keep the thimble hot. The insoluble fraction remained in the thimble, while the soluble fraction was recovered after evaporation of the solvent; the proportion of each fraction is reported in Table 1. After each extraction, the polymer was treated again with Santonox, filtrated, and dried overnight under vacuum at 40 °C.

Synthesis of Glycidyl Azide Polymer. *Caution!* This synthesis should be accomplished behind a protective shield.

Table 1. Characterization of Unfractionated Isotactic ((*RS*)-PECH) and Chiral ((*S*)- and (*R*)-PECH) Poly(epichlorohydrin)s and Their Soluble and Insoluble Fractions

PECH	yield[a] (%)	M_w (kg/mol)	isotacticity (%)	T_m (°C)	ΔH_m (J/g)
(*RS*)-PECH	90[b]	1150	80	117	31
insoluble	59[c]	1700	88	124	44
soluble	24[d]	540	72	109	6
(*S*)-PECH	74[b]	560	100	121	62
insoluble	82[c]	690	100	125	65
soluble	17[c]	200	92	114	40
(*R*)-PECH	76[b]	150	100	118	56
insoluble	77[c]	570	*e*	124	61
soluble	23[c]	60	*e*	108	36

[a] After AcAc and antioxidant treatments. [b] Of unfractionated PECH, relative to ECH. [c] Of soluble and insoluble PECH, relative to unfractionated PECH. [d] 40% after fractionation; 24% after fractionation and treatment with antioxidant. [e] Not available.

PECH (10.0 g, based on 0.108 mol of epichlorohydrin) and dimethylformamide (120 mL) were introduced in a two-neck round-bottom flask equipped with a condenser, a magnetic stirrer, and a septum. The reaction mixture was heated slowly until the polymer was completely dissolved (60−70 °C). To this solution was added 8.4 g (0.13 mol) of sodium azide, and the temperature was raised to 95 °C. After a given reaction time, the mixture was allowed to cool, the salts were filtrated, and the solvent was evaporated. The resulting GAP was dissolved in chloroform, washed three times with salted water, dried over $MgSO_4$, and filtrated. Complete evaporation of chloroform yielded 9.6 g of GAP (90% yield, calculated from the molar ratio of epichlorohydrin and 1-(azidomethyl)oxirane).

Polymer Characterization. Molecular weight measurements of PECHs were determined by viscosimetry in 1-chloronaphthalene at 100.0 °C. An Ubbelohde viscosimeter was used and PECH concentrations were varied between 0.5 and 5 g/L. The molecular weights were calculated using eq 2 where $[\eta]$ represents the intrinsic viscosity of the specific polymer−solvent system, and M_w the weight-average molecular weight of PECH:

$$[\eta] = 8.93 \times 10^{-5} M_w^{0.731} \quad (2)$$

This equation can be equally applied to atactic and isotactic PECH.[4]

The molecular weights of GAP were determined by gel permeation chromatography (GPC) in tetrahydrofuran at 28 °C and 1 mL/min using a Waters chromatograph (Waters 712 WISP) equipped with a programmable HPLC pump (Waters 590), an automatic sample injection module, and a differential refractometer (Waters 410). The Maxima 820 chromatography station was used to acquire and process the data. The calibration was performed with polystyrene standards on Ultrastyragel columns.

Differential scanning calorimetry measurements were conducted with a DSC 2910 apparatus from Dupont Instruments equipped with a Dupont Thermal Analyst 2100. The calibration was done with indium (156.6 °C) and biphenyl (69.3 °C), and the scan rate was fixed at 20 deg/min. Melting temperatures were recorded at the end of the melting peak.

The isotacticity of PECH and GAP was evaluated from ^{13}C nuclear magnetic resonance measurements, using a Bruker AC-300 operating at 75.5 MHz. PECH was dissolved in deuterated dimethyl sulfoxide at a concentration of 0.1 g/mL, and the spectra were recorded at 80 °C with a 0.442 s acquisition time, a 1 s delay time, and a standard spectral width of 18 500 Hz. The isotacticity of GAP could only be evaluated with high-resolution spectra, recorded at room temperature with a 3.4 s acquisition time, no delay time, and a spectral width of 4800 Hz; the polymers were dissolved in deuterated chloroform (100 g/L). The azidation degrees of GAP were also determined by ^{13}C NMR spectroscopy, using a Bruker WP 200 Sy or a Varian XL-200, both operating at 50.3 MHz with a 1 s acquisition time; deuterated chloroform was used as the solvent. A variation of 1% of the azidation degree was detected for delay times of 0−10 s. Given this small variation, all the spectra of partially or completely azidated PECHs were recorded with a delay time of 0 s. The azidation degree was calculated from the relative area of the azidomethyl and the chloromethyl peaks at 52.22 and 44.14 ppm, respectively.

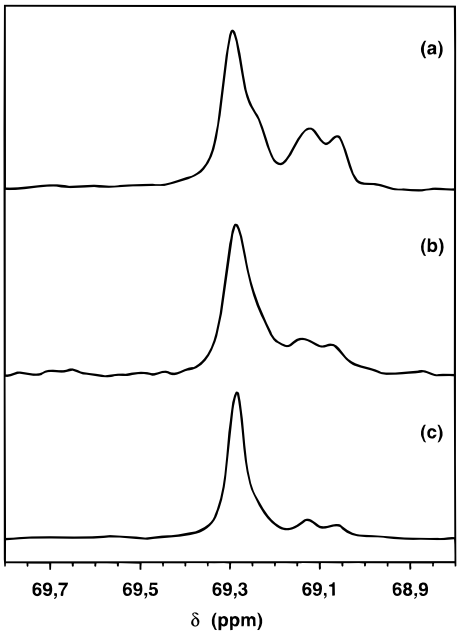

Figure 1. Expansion of the methylene carbon region of the ^{13}C NMR spectra of unfractionated treated (*RS*)-PECH (b) and of the soluble (a) and insoluble (c) fractions isolated by fractionation.

The optical rotation angles were measured with a Jasco DIP 300 polarimeter operating at 589 nm. Measurements were done at room temperature in tetrahydrofuran at a concentration of approximately 10 g/L (see Table 3).

Results and Discussion

Poly(epichlorohydrin). Isotactic (*RS*)-PECH, obtained from the polymerization of racemic epichlorohydrin, has been extracted with acetone to yield a soluble and an insoluble material. The tacticity, crystallinity, and molecular weight of each PECH fraction, including the unfractionated polymer, have then been evaluated. The same treatment has been applied to chiral (*S*)- and (*R*)-PECH, prepared from the corresponding optically active epichlorohydrin. Table 1 summarizes the characteristics of all PECH samples.

The proportion of soluble (*RS*)-PECH isolated after fractionation with acetone is 40% and drops to 24% after the treatment with the antioxidant (Table 1). In contrast, the proportion of soluble polymer in chiral PECHs is smaller than in (*RS*)-PECH and does not noticeably vary when treated with the antioxidant. It can also be seen that the molecular weights of the insoluble PECH fractions are all slightly higher than those of the unfractionated polymer samples, while the soluble fractions are all characterized by much lower molecular weights (Table 1).

Figure 1 shows the expanded methylene carbon region of the ^{13}C NMR spectra of each fraction of (*RS*)-PECH. The major peak at 69.30 ppm is assigned to isotactic (*RR* and *SS*) sequences and the minor peaks, at 69.15 and 69.10 ppm, to racemic (*RS* and *SR*) sequences. These assignments are based on the ^{13}C NMR spectra of (*R*)- and (*S*)-PECH, shown in Figure 2, which are characterized by the presence of a single peak at 69.30 ppm in the methylene carbon region. This peak can only be attributed to isotactic sequences, since only one

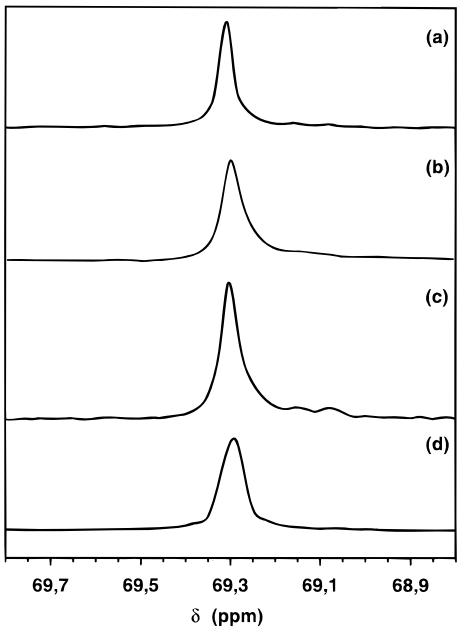

Figure 2. Expansion of the methylene carbon region of the ^{13}C NMR spectra of the unfractionated treated (*R*)-PECH (a) and (*S*)-PECH (b) and of the soluble (c) and insoluble (d) fractions of treated (*S*)-PECH isolated by fractionation.

of the epoxide bonds (CH_2-O) is cleaved during the polymerization reaction;[5,6,26,27] the configuration of the asymmetric carbon atom thus remains the same. The degree of isotacticity of the unfractionated (*RS*)-PECH samples is around 80%, while it drops to 72% for the soluble fraction (Table 1). The isotacticity of the insoluble fraction is however increased to 88%. As predicted,[5,6,26,27] (*S*)- and (*R*)-PECH are completely isotactic, as can be noticed from a close examination of Figure 2 (see also Table 1). However, two small peaks are detected at the chemical shift associated with racemic sequences (69.15 and 69.10 ppm) in the soluble fraction of (*S*)-PECH (Figure 2c), corresponding to a degree of isotacticity of 92% (Table 1). The NMR spectra of the soluble and insoluble fractions of (*R*)-PECH, not shown in Figure 2, are similar to those of (*S*)-PECH.

Figure 3 shows the DSC melting curves of each fraction of isotactic and chiral PECHs; the corresponding melting temperatures and enthalpies of fusion are reported in Table 1. The thermograms of the unfractionated PECH samples (Figure 3b,e,h) are characterized by double melting peak endotherms, similar to those already reported in the literature.[28−30] Multiple melting peaks are common in some polymeric systems[31] and are generally related to the presence of several crystal sizes, perfection, and/or internal order. However, unlike (*RS*)-PECH, in which the relative proportion of the high and low melting peaks is comparable (Figure 3b), the main peak of the chiral polymers is undoubtedly the high melting one; the peak maximum is also higher (109 vs 112 °C), while the low melting peak maximum remains the same (98 °C). The enthalpies of fusion of the chiral polymers, between 56 and 62 J/g, are higher than the one of (*RS*)-PECH (31 J/g); their melting temperatures are also higher (Table 1).

The extraction splits PECH into two fractions of different melting temperatures and crystallinity. The DSC thermograms of the insoluble fractions (Figure 3c,f,i) show that the intensity of the high melting peak (114−117 °C, peak maximum) is largely increased as compared with that of the unfractionated polymer sample, while the low melting endotherm is reduced to a shoulder of the main peak at approximately 88 °C (peak maximum) for (*RS*)-PECH (Figure 3c) and even completely disappears for chiral PECHs (Figure 3f,i). The melting temperatures of all the insoluble fractions (124−125 °C) are comparable and higher than those of the starting PECH (117−121 °C) (Table 1). The fractionation also induces a significative increase of the enthalpy of fusion from 31 to 44 J/g for the insoluble (*RS*)-PECH (Table 1); a smaller increase of approximately 3−5 J/g is detected for chiral PECHs.

Figure 3 also shows that the melting curves of the soluble fractions of PECHs (Figure 3a,d,g) are all characterized by double melting endotherms and low enthalpies of fusion and melting temperatures compared to the starting PECH samples. The enthalpies of fusion of the soluble fractions of (*S*)- and (*R*)-PECH, 40 and 36 J/g, respectively, are higher than the one of (*RS*)-PECH (6 J/g) but lower than those of the unfractionated (*R*)- and (*S*)-PECH (62 and 56 J/g, respectively) (Table 1).

Thus, as already reported,[4,30] the polymerization of racemic and chiral epichlorohydrin using $AlEt_3/H_2O$ produces a semicrystalline polymer of high molecular weight. The degree of crystallinity, calculated by the ratio of the enthalpy of fusion of the polymer to that of a perfectly crystalline sample[29] (143.6 J/g), is evaluated as 22% for the unfractionated (*RS*)-PECH. Since the atactic polymer is completely amorphous, the crystallinity of the polymer is due mainly to its isotacticity, estimated by NMR at 80% (Table 1). When chiral monomers are used, a completely isotactic polymer having a degree of crystallinity around 40% is obtained for the unfractionated (*S*)- or (*R*)-PECH.

The extent of crystal formation (related to ΔH_m) and the stability and internal ordering of the PECH crystals (related to T_f) are very sensitive to the isotacticity of the polymer chains. The higher isotacticity of the chains of the chiral PECHs compared with (*RS*)-PECH leads to a greater ordering of the polymer chains in the crystalline form and to more stable crystals, which is shown by a greater enthalpy of fusion and melting temperatures for the chiral polymers. As expected,[4] the fractionation of isotactic PECH allows the isolation of an insoluble material of higher molecular weight, crystallinity, and isotacticity than the starting material and of a soluble fraction of much lower molecular weight, crystallinity, and isotacticity. The insoluble material isolated after fractionation of (*RS*)-PECH is not as crystalline as the unfractionated chiral PECH samples but has a higher melting temperature, comparable to those of the insoluble chiral PECHs. Thus, although the proportion of crystalline material in (*RS*)-PECH is not as important as in chiral PECH, the isotacticity of the polymer chains is high enough to allow the crystals to reach a degree of internal order similar to that of the chiral PECHs.

Also, as can be seen from the thermograms of Figure 3 and the results of Table 1, the fractionation of chiral (*R*)- and (*S*)-PECH withdraws from the bulk polymer a material of intermediate molecular weight and crystallinity, thus leaving an insoluble PECH characterized by a higher molecular weight and crystallinity than the starting material. However, since chiral PECHs are considered completely isotactic, the properties of the polymer should not be affected by the extraction. This unexpected result may be explained by the degree of isotacticity of 92% found for the soluble (*S*)-PECH, which indicates the presence of some defects in the polymer chains, which usually cannot be detected in unfractionated samples because of their low concentra-

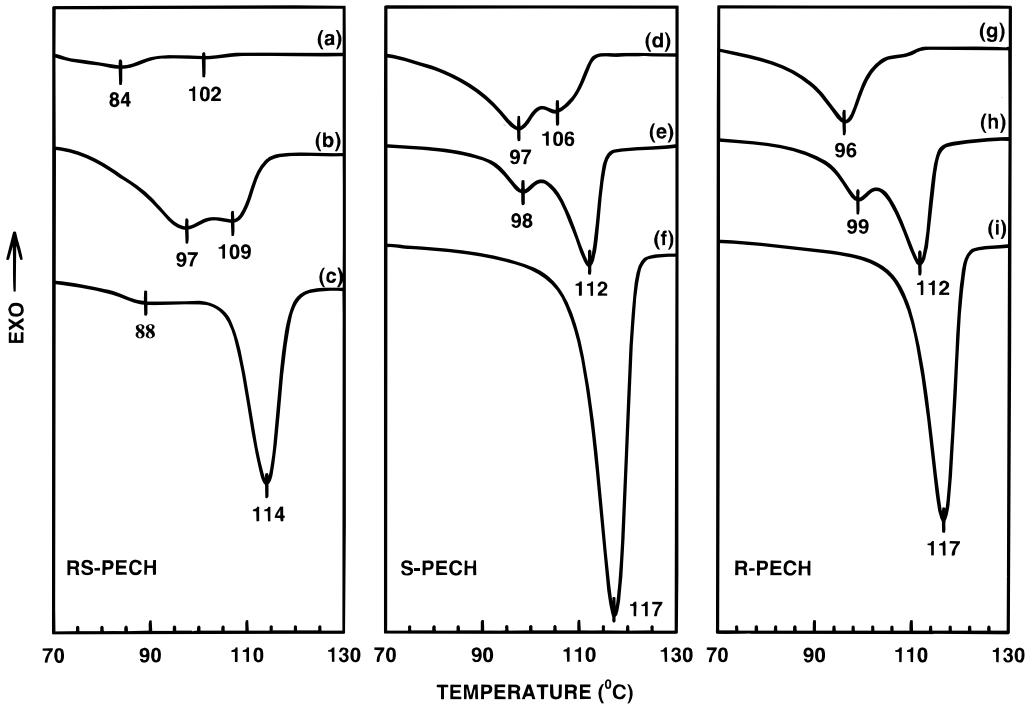

Figure 3. DSC curves of the unfractionated (b,e,h) isotactic ((*RS*)-PECH) and chiral ((*S*)- and (*R*)-PECH) poly(epichlorohydrin)s and of their soluble (a,d,g) and insoluble (c,f,i) fractions.

tion. Indeed, the soluble fraction constitutes only 17% of the whole polymer sample, which corresponds to a proportion of approximately 1% of defects in the chains (8% × 17%). These defects are probably due to the presence of a small proportion of molecules of *R* configuration in the (*S*)-epichlorohydrin (according to the supplier, the optical purity of (*R*)- and (*S*)-epichlorohydrin is 97%); they may also come from an imperfection of the polymerization process.

It has also been observed that the proportion of soluble (*RS*)-PECH isolated after extraction with acetone (40%) drops to 24% after treatment with an antioxidant, while no such decrease has been noticed for the chiral PECHs. This puzzling fact may be tentatively explained by a partial degradation of the soluble (*RS*)-PECH during the extraction process in a methanol-soluble low molecular weight material that cannot be isolated in the subsequent treatment with the antioxidant. This treatment consisted in a 90 min agitating period of the polymer in a 0.2% methanol solution of antioxidant, followed by isolation of the polymer by filtration. If the degraded PECH is methanol-soluble, it cannot be recovered from the antioxidant solution. The different behavior observed for chiral PECH samples could suggest a better stability against degradation. This hypothesis is supported by the observation that the rate of degradation of solid chiral PECHs appears slower than that of solid (*RS*)-PECH, based on the aspect and odor of PECH samples kept for a long time at room temperature without antioxidant.

Glycidyl Azide Polymer. Isotactic glycidyl azide polymers have been synthesized using unfractionated (*RS*)-PECH as the starting material. The molecular weights of some PECHs having different azidation degrees are reported in Table 2. The azidation is generally completed after approximately 6 h of reaction. The reaction proceeds slightly faster when an excess of NaN_3 of 20% is used. The high azidation rate observed at the beginning of the reaction decreases gradually as the reaction progresses.

Table 2. Characterization of (*RS*)-GAP Obtained from the Reaction of Unfractionated Treated (*RS*)-PECH with an Equimolar[a] Ratio or an Excess[b] of 20% of NaN_3

azidation time (h)	azidation[a] (%)	azidation[b] (%)	M_w [a] (kg/mol)	M_w/M_n [a]	M_w [b] (kg/mol)	M_w/M_n [b]
0	0	0	1150[c]		1150[c]	
2	59	64	546	4.7	497	4.5
4	82	87	457	4.3	306	3.0
6	89	100	164	2.3	307	4.1
24	100	100	139	2.3	105	2.6
48	100	100	194	2.4	177	2.2
96		100			100	2.3

[a] NaN_3/ECH = 1.0. [b] NaN_3/ECH = 1.2. [c] M_w of PECH by viscosimetry measurements; all others by GPC.

Table 3. Characterization of (*R*)- and (*S*)-GAP Obtained from the Reaction of Unfractionated Treated (*R*)- and (*S*)-PECH, Respectively, with an Equimolar Ratio of NaN_3

GAP	M_w [a] (kg/mol)	M_w/M_n	$[\alpha]_D^{25}$ [b] (deg)
S	132	3.0	42
R	85	3.5	−40

[a] By GPC. [b] Concentration of (*S*)- and (*R*)-GAP of 9.74 and 16.89 g/L, respectively (in THF).

Table 2 also shows that the molecular weight of PECH decreases significantly during the azidation process, going from approximately 1000 to 100 kg/mol. When the azidation is completed, the molecular weight of the polymer seems to vary randomly between 100 and 307 kg/mol, no general inclination toward an increase or a decrease of the molecular weight being detected. The polydispersity also tends to decrease as the azidation progresses, going from approximately 4.5−4.7 to 2.2−2.4.

The azidation has also been performed on unfractionated chiral PECH samples, using an excess of NaN_3 of 20% and a reaction time of 24 h. The results for completely substituted (*R*)- and (*S*)-GAP are reported in Table 3. (*S*)-GAP is characterized by a molecular weight of 132 kg/mol and a polydispersity of 3.0; for (*R*)-GAP, these values are of 85 kg/mol and 3.5, respectively. Both polymers are optically active. (*R*)-GAP has a

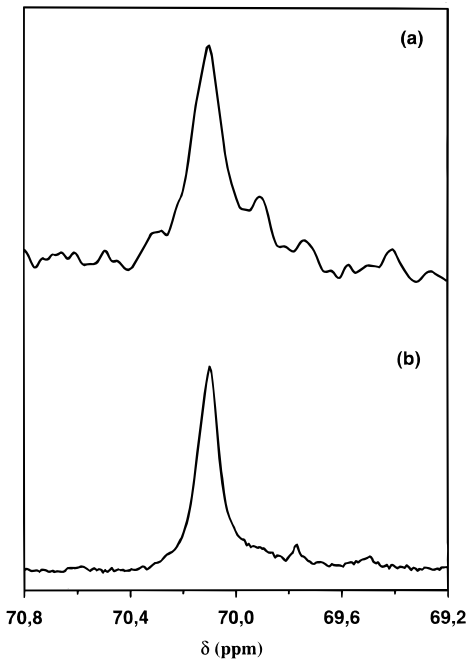

Figure 4. Expansion of the methylene carbon region of the ^{13}C NMR spectra of (*RS*)-GAP (a) and (*R*)-GAP (b).

slightly lower optical rotation angle than (*S*)-GAP, but nevertheless of the same magnitude and, as expected, of opposite sign.

Figure 4 shows the expanded ^{13}C NMR spectra of (*RS*)- and (*R*)-GAP; the spectrum of (*S*)-GAP, not presented here, is similar to that of (*R*)-GAP. Only the peak at 70.10 ppm, attributed to the isotactic sequences of the backbone methylene carbon atoms, is stereosensible. For (*RS*)-GAP, two additional small peaks are detected around the main peak at 69.80 and 70.30 ppm; these peaks are related to the presence of a few racemic sequences on the polymer backbone.

The azidation of (*RS*)-PECH and of the chiral samples induces a decrease of the glass transition temperature from −20 to −35 °C. None of the DSC curves of the obtained GAPs shows a melting endotherm.

Thus, high molecular weight (*RS*)-, (*R*)-, and (*S*)-GAPs can be produced by substituting each chlorine atom located on the chloromethyl pendant groups of PECH by azide groups. The drop of the polymer molecular weight from 1000 to 100 kg/mol (Table 2) suggests that the polymer backbone is degraded during the reaction. The decrease of the polydispersity could indicate that the cleavage occurs mainly at the longer chains, thus leaving in solution chains of comparable but lower molecular weight. The extent of degradation is however hard to establish because, on the one hand, the molecular weights of PECH and GAP have not been measured by the same method (viscosimetry and GPC, respectively) and, on the other hand, none of these methods gives an absolute molecular weight. The choice of method is limited by the low solubility of isotactic PECH in common organic solvents. A straightforward comparison of the molecular weight of PECH and GAP thus cannot be established. However, considering the large difference in molecular weights, the occurrence of degradation must be considered seriously. This phenomenon is supported by the results of many authors, who report that PECH degrades when it is submitted to a nucleophilic substitution reaction.[11,12,14,16,17] For example, Nuyken et al.[14] also observed an important degradation of the polymer backbone accompanied by a decrease of the polydispersity for the modification of PECH with benzenesulfonyl or *p*-toluenesulfonyl groups. Vandenberg[16] proposed that the cleavage of PECH with bases such as sodium hydroxide and sodium methoxide at moderated temperatures (>65 °C) occurs via abstraction of a proton from the backbone methylene group followed by chain scission and expulsion of a chlorine ion to form a carbonyl and an allyl ether end, which is further hydrolyzed by acid to an alcohol with an aldehyde as byproduct. The extent of PECH degradation could possibly be reduced by conducting the reaction at a lower temperature, but the azidation is then incomplete.

It has been noted that GAP molecular weight increases slightly after 48 h of reaction (Table 2). Moreover, the solubility of some samples also decreases, sometimes even to the point where a complete solubilization becomes impossible. These results suggest that the azidation of PECH induces a slight cross-linking or branching of the polymer chains. A similar situation has already been reported for the modification of PECH with unsaturated potassium carboxylates[11] and thiocyanates.[14] In these two cases, the cross-linking of the chains occurred when long reaction times were employed. The azidation of PECH indeed induces an increase of the polymer molecular weight after 48 h of azidation, but longer reaction times (96 h) do not favor additional cross-linking or branching, at least with the experimental conditions used (Table 2). It has been suggested[12,32] that the cross-linking of the polymer may be due to the polymerization of the allyl ether groups formed during the substitution reaction.

(*RS*)-GAP is highly isotactic, as seen from the relative intensity of the isotactic sequences peak of the methylene group (70.10 ppm) to those of the racemic sequences (69.80 and 70.30 ppm) (Figure 4a). The actual degree of isotacticity is however hard to establish, due to the superposition of the peaks. For (*R*)-GAP (Figure 4b), a few racemic sequences are detected, indicating that this polymer is almost completely isotactic, as is the starting PECH. The similarity of the optical rotation angles of (*R*)- and (*S*)-GAP also supports this affirmation. Thus, the isotacticity of the polymer is not affected by the azidation of the chloromethyl groups. The lower optical rotation angle of (*R*)-GAP may be due to the fact that one enantiomer is often less pure than the other, thus leading to a polymer of lower isotacticity and crystallinity; this can also explain the lower enthalpy of fusion of the unfractionated (*R*)-PECH as compared to that of the corresponding (*S*)-PECH (56 versus 62 kJ/mol).

In contrast with isotactic PECH, and despite the high isotacticity of the GAPs, none of the samples obtained are crystalline, as indicated by the lack of melting peaks on the DSC curves. The origin of this absence of crystallinity is however unknown. The azide group, larger than the chlorine atom, may hinder the arrangement of the chains in the crystalline structure characteristic of PECH; it may also be not electron-attracting enough to induce strong intermolecular interactions between GAP chains and induce crystallization. If branching or cross-linking does indeed occur, the regularity of the chains may be sufficiently disturbed to prevent the crystallization of GAP.

Therefore, a highly isotactic GAP of high molecular weight can be synthesized by the modification of PECH obtained by the Vandenberg process;[4] completely isotactic, chiral GAP can also be obtained if chiral PECH is used as the starting material. The azidation does not affect the isotacticity of the chains but induces a marked decrease of the polymer molecular weight; nevertheless,

a GAP of high molecular weight (100 kg/mol) is still produced. Some branching or cross-linking may also occur when long reaction times are used. No crystallinity has however been detected in any GAP sample, including the chiral polymers.

Summary and Conclusions

The polymerization of racemic epichlorohydrin with $AlEt_3/H_2O$ leads, as in the Vandenberg process,[4] to the formation of a highly isotactic polymer of high molecular weight; a completely isotactic, chiral polymer is obtained when a chiral monomer is employed. As expected, the insoluble (*RS*)-PECH isolated by fractionation has a higher molecular weight, crystallinity, and isotacticity than the unfractionated polymer sample; the soluble fraction has a much lower molecular weight and is almost completely amorphous despite a degree of isotacticity of 72%. The fractionation of chiral PECH also splits the polymer into a soluble and an insoluble fraction, the proportion of soluble polymer being however much lower than for (*RS*)-PECH. The soluble chiral PECH has a degree of isotacticity of 92% and is more crystalline than the unfractionated (*RS*)-PECH. The fractionation thus withdraws from chiral PECH incompletely isotactic chains coming either from the presence of a few monomers of opposite configuration in chiral epichlorohydrin or from an imperfection in the polymerization process. The insoluble chiral PECH remaining is isotactic enough to give rise to a single peak endotherm in DSC, suggesting a better homogeneity of the polymer crystals; this can have important consequences on crystallization kinetics and morphological studies.

The azidation of PECH produces GAP without altering the isotacticity of the polymer chains; highly isotactic and completely isotactic, optically active GAPs can thus be produced. The molecular weight drops however sharply during the azidation process, indicating that degradation of the polymer backbone occurs during the reaction; a polymer of high molecular weight is still obtained. For long reaction times, an increase of the polymer molecular weight is also noticed, probably because of a slight cross-linking or branching of the polymer chains. No crystallinity is detected in any GAP sample. This lack of crystallinity may be due to the azide group, larger and less electronegative than the chlorine atom, although the presence of some branched or cross-linked structures, even in low density, would probably be sufficient to hinder the crystallization of a polymer that would otherwise be semicrystalline.

In conclusion, this study reports for the first time the synthesis and some properties of isotactic and chiral GAPs of high molecular weight. Despite the degradation occurring during the azidation of PECH, the isotacticity of the polymer chains remains intact, but the GAPs are not crystalline. This study also reports the properties of isotactic and chiral PECHs used as starting materials for the synthesis of GAPs. It has been found that chiral PECH can be fractionated to remove the small proportion of incompletely isotactic chains coming from impurities of opposite configuration in the monomer or a defective polymerization process. The homogeneity of the crystals remaining in the insoluble fraction is thus enhanced, and the crystallinity and melting temperatures of the polymer increased enough to be taken in consideration in eventual crystallization kinetics or morphological studies of chiral PECH.

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