

Synthesis, Crosslinking, and Characterization of Energetic Polymers through the Azidification of Glycidyl Ether Prepolymers

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ABSTRACT: Low-molecular-weight atactic poly(propylene oxide) and poly(epichlorohydrin) (PECH) were chlorinated on average up to 4.42 chlorine atoms per repeat unit. A study of the products showed that chlorine substitution preferentially occurred on already chlorinated repeat units, yielding chlorine -rich and chlorine -poor sequences. As the extent of chlorine substitution increased, the glass-transition temperature of the polymers markedly increased, and their solubility in most of the organic solvents drastically decreased. The chlorinated polymers were azidified with NaN_3 in dimethyl sulfoxide solutions. An analysis showed that azide groups replaced 99.8–99.9% of the initially present chlorine atoms. As the azide content of the samples increased, initially opaque polymers become dark brown, and their solubility increased in water but decreased in organic solvents. Samples with approximately four or more azide

groups per repeat unit were only soluble in dimethyl sulfoxide and water. The standard enthalpy of formation of the polymers became increasingly positive as the azide content increased. The enthalpy of formation of a sample with 4.42 N_3 /repeat unit was 6929 kJ/repeat unit, whereas this value was only 103 kJ/mol for classical GAP. An azidified sample from PECH (4.42 N_3 /repeat unit) was crosslinked with a commercial triisocyanide into a rubbery product. The density and ultimate tensile strength of the rubbery product were 1.44 g/cm³ and 4.84 MPa, and it swelled about 10% at 20°C in water. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3785–3790, 2004

Key words: crosslinking; thermal properties; mechanical properties; calorimetry; NMR

EXPERIMENTAL

Materials

All solvents were purified by fractional distillation.

Poly(propylene oxide) (PPO) was synthesized as described by Steiner et al.¹ The number-average molecular weight of PPO was 4000, which was calculated by end-group determination. Poly(epichlorohydrin) (PECH) was obtained from 3M Co.

Chlorine gas was obtained from the oxidation of NaCl with KMnO_4 . The reaction flask was flushed with N_2 gas before the addition of concentrated H_2SO_4 (ca. 40 wt %). Excess chlorine was absorbed in aqueous NaOH solutions.

Procedure

The chlorination of the polymers were achieved by the bubbling of Cl_2 gas into solutions of the polymers in carbon tetrachloride (2.5 wt %) at 60°C for several days. The rate of chlorination apparently increased with the intensity of sunlight, the partial pressure of

Cl_2 , and the temperature. However, at temperatures higher than 60°C, because of the decrease in the solubility of Cl_2 , the rate of reaction slowed down. At the end of the chlorination, the solvent was distilled off, and the residue was extracted with benzene and neutralized with aqueous NaHCO_3 . Finally, the benzene solution was washed with distilled water and freeze-dried.

The extent of chlorination was determined from both the stoichiometry of the reaction, through the measurement of the increase in the mass of the polymer, and the volumetric determination of chloride anions by Mohr's method. For the conversion of the covalently bound chlorine atoms into an ionic form, 3–25-mg samples in filter paper envelopes were burned in an atmosphere of O_2 .² To test the reliability of this method, we analyzed *m*-chloronitrobenzene ($\text{C}_6\text{H}_4\text{NO}_2\text{Cl}$; 22.5% chlorine), and the chlorine content of this compound was found to be 23.7%. We expected that this combustion technique would fail in hydrogen-poor samples. Indeed, the chlorine content of CCl_4 (92.2% chlorine) was found to be only 25%. During the burning of CCl_4 , hydrogen from the cellulose envelope converted covalent chlorines into HCl. To provide a hydrogen-rich medium, we dissolved CCl_4 in molten wax paraffin at 70°C (35% CCl_4). This mixture was solidified at room temperature, and a

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sample of this mixture was analyzed. The percentage of chlorine of CCl_4 according to this paraffin method was 78%. The large error involved in this determination was probably due to the vaporization of some CCl_4 during the solution process and the necessity of using very small quantities of the samples (25 mg; if larger amounts were used, explosions were possible). The chlorine contents of chlorine-rich polymers were determined with both classical and paraffin methods.

The azidification of the chlorinated polymers was achieved in dimethyl sulfoxide (DMSO) solutions (25–50 g/L) at 95°C with excess NaN_3 . The reactor was swept with N_2 , and the reaction mixture was stirred. After a reaction time of 2 days, azidified polymers (AZPs) were isolated from the reaction mixture. According to the azide contents of the products, two different isolation procedures were used.

1. AZP with a low azide content ($<3 \text{ N}_3/\text{repeat unit}$): Upon the addition of excess CCl_4 into the reaction mixture (3 volumes of CCl_4 for 1 volume of the reaction mixture), three phases appeared. The solid phase contained NaN_3 and NaCl , the CCl_4 -rich phase contained only a fraction of AZP, and the DMSO-rich phase contained considerable amounts of salts, the rest being AZP. AZP in the CCl_4 phase was isolated by the evaporation of the solvent. However, the evaporation of the solvent from the DMSO-rich phase left a mixture of AZP with salts. AZP from this mixture was extracted with acetonitrile (or tetrahydrofuran). Finally, AZPs from different sources were combined. We also synthesized and isolated classical GAP according to a literature recipe;³ however, the procedure described here was quicker and gave a higher yield ($>92\%$) than the literature value (72%).
2. AZP with a high azide content ($>3 \text{ N}_3/\text{repeat unit}$): AZPs with high azide contents were insoluble in organic solvents (acetone, acetonitrile, CCl_4 , benzene, and tetrahydrofuran) but soluble in water and DMSO. Therefore, the aforementioned procedure was not applicable to these products. For the isolation of these products, DMSO was completely evaporated, and the residue was dissolved in 250 mL of water. In some products (especially daughter products of PECH), there were also water-insoluble fractions. These fractions were separated by filtration and were free of any salts. The aqueous solution was successively treated with anion and cation exchangers until the depletion of Na^+ , Cl^- , and N_3^- ions. Water was evaporated with a Rotavapor instrument. Finally, residual AZP was dried at 95°C and 10^{-3} Torr for 12 h.

AZPs were cured with a commercial trifunctional isocyanide, Desmodur N-100, at 40°C. Crosslinking

ratios of 0.9–1.2 mol/mol were used. The extent of crosslinking was tested by the determination of the water-soluble fraction of the cured products. For this purpose, 0.25-g samples were extracted with 30 cm^3 of water at room temperature for 2 days.

Characterization of the polymers

The molar masses of the polymers were determined with cryoscopy (in benzene or in DMSO) and end-group analysis under the assumption that the chains were linear and contained either hydroxyl groups or double bonds at the chain terminals. The contents of double bonds were determined by an iodine monochloride procedure,⁴ and the contents of hydroxyl groups were determined by esterification with phthalic anhydride.¹

Infrared measurements were taken with a 510 Fourier transform infrared spectrometer with KBr pellets of glassy polymers (highly chlorinated PPO and PECH) or smeared NaCl windows of oily polymers (PPO, PECH, and AZPs).

A Bruker Spectroscopin Avance DPX 400 Ultra instrument was used for ^{13}C -NMR measurements. Deuterated chloroform for low-azide-content polymers and water for high-azide-content polymers were used as solvents.

Pyrolysis mass spectrometry and DPMS analysis were performed with a 5973HP quadrupole mass spectrometer and a direct insertion probe. The ionization energy was adjusted to 70 eV. The heating rate was 445°C/min, and the scanning rate was 2 scan/min.

General V4.1c DuPont 2000 and PL TGA 1500 instruments were used for the thermal characterization of the products under an atmosphere of N_2 . The scanning rate of the devices was adjusted to 10°C/min.

Tensile strength measurements were performed with a Lloyd LS500 tensile testing machine at room temperature. The gauge dimensions were 30 mm \times 8 mm \times 1 mm.

The density of the cured products was measured with a pycnometer in benzene at 20°C.

The rubbery products were allowed to swell in water at 20°C for 2 days. The percentage of swelling was calculated from the dry and swollen masses under the assumption that the densities of rubbers and water were constant.

Higher values of the heat of combustion of AZPs were calculated from measured values of the internal energy changes in a Parr bomb calorimeter. Oily polymer samples were burned in polyethylene envelopes of known masses. The heats of combustion of the envelopes were measured in independent experiments. For the calculation of the enthalpy of formation of a repeat unit of AZP, all reactants and products of combustion were assumed to be in their standard state.

TABLE I
Chlorination of PPO and PECH

Experiment	Product	Reaction time (h)	Cl/ru ^a	Cl/ru ^b	Cl/ru ^c
1	CIPPO-0.79	6	0.79	0.84	0.83
Test	PECH	—	—	0.89	0.99
2	CIPPO-1.16	6	1.16	—	—
3	CIPPO-1.64	8	1.64	—	—
4	CIPPO-2.30	20	2.30	—	—
5	CIPECH-2.50	—	2.50	—	—
6	CIPPO-3.16	36	3.16	1.48	3.10
7	CIPPO-3.18	24	3.18	—	—
8	CIPECH-3.50	12	3.50	—	—
9	CIPPO-3.83	54	3.83	3.69	3.93
10	CIPECH-4.32	28	4.32	3.68	4.22
11	CIPECH-4.42	—	4.42	—	—

^a Cl/ru (moles of Cl per moles of repeat unit) value from stoichiometry.

^b Cl/ru from direct combustion.

^c Cl/ru from combustion in paraffin.

RESULTS AND DISCUSSION

Through the chlorination of PPO and PECH, several chlorinated glycidyl ether polymers were obtained from PPO and PECH. The chlorinated polymers and azidified polymers are denoted CIPPO-*X*, CIPECH-*X*, AZPPO-*X*, and AZPECH-*X*, depending on the parent polymer (PPO or PECH). *X* represents the average number of chlorine atoms or azide groups per repeat unit. The reaction conditions and obtained products are listed in Table I.

In experiments with comparable reaction conditions (experiments 6 and 10 and experiments 4 and 8 in Table I), the same amount of chlorine substitution per repeat unit of the polymer occurred more quickly in PECH than in PPO. This observation was consistent with the view that as the repeat units became richer in chlorine with a decreasing hydrogen population, the remaining hydrogen atoms in these repeat units became more susceptible to chlorine attack. This observation was further supported by mass spectrometry⁵ and ¹³C-NMR measurements. Mass spectra of CIPPO-0.79 resembled those of PPO rather than PECH; a large number of repeat units were intact, and this indicated that chlorine atoms were gathered on some of the repeat units. Even in chlorine-rich samples, such as CIPPO-3.83, some weak peaks due to PPO repeat units were observed, but peaks of CCl₃⁺ and CHCl₂⁺, along with repeat units with 5 or 6 chlorine atoms and dimeric blocks of repeat units with 5, 6, 7, or 8 chlorine atoms, were dominant.

¹³C-NMR spectra of the chlorinated polymers were interpreted with an empirical equation relating the chemical shift of a carbon atom (α_C) to the number of chlorine atoms on it as well as chlorine atoms on the next neighbor (β_C) and one after the next neighbor (γ_C):⁶

$$\delta \text{ of } \alpha_C (\text{ppm}) = A + 31 \times n^\alpha + 10 \times n^\beta - 5.1 \times n^\gamma \quad (1)$$

where n^α , n^β , and n^γ are the number of chlorine atoms on α , β , and γ carbon atoms, respectively. *A* is the chemical shift of α_C (methyl carbon) in PPO.

Assignments according to eq. (1) are summarized in Table II.

On the basis of these results, we can conclude the following:

1. All the hydrogen atoms in a repeat unit of PPO and PECH can be substituted with chlorine atoms.
2. Because the hydrogen atoms become more reactive as the population of chlorine atoms increases in a repeat unit, the chlorinated polymers have chlorine-rich and chlorine-poor repeat units.

The infrared spectrum of the chlorinated samples showed carbonyl absorption between 1635 and 1790 cm⁻¹, which was absent in the parent polymers. The appearance of carbonyl peaks was indicative of the oxidative degradation of polymer chains, which accompanied chlorination. To avoid oxidation, we performed the chlorination of the polymers under N₂ gas. Although the relative intensity of the carbonyl groups synthesized under N₂ gas markedly decreased, it did not completely disappear. For the estimation of the extent of degradation, the molar masses of PECH, CIPECH-2.50, CIPECH-4.42, and AZPPECH-4.42 are compared in Table III. The ratio of the hydroxyl functionality (F_{OH} ; i.e., the moles of hydroxyl groups per gram of the polymer times 10⁴) to the double-bond functionality (F_{DB} ; i.e., the moles of double bonds per

TABLE II
Distribution of Cl Atoms in Samples Estimated from Eq. (1)⁶

Sample	Absorption of α_C	β neighbor	γ neighbor	Intensity ^a
CIPPO-0.79	CH ₃ at 17 ppm	CH	CH ₂	w
	CH ₃ at 13 ppm	CH	CHCl	w
	CH ₃ at 24 ppm	CCl	CHCl	m
	CH ₃ at 29 ppm	CCl	CH ₂	s
	CH ₂ Cl at 53 ppm	CCl	CH ₂	m
CIPPO-3.83	CHCl ₂ at 65 ppm	CH	CHCl	m
	CHCl ₂ at 68 ppm	CCl	CCl ₂	w
	CHCl ₂ at 73 ppm	CCl	CHCl	m
	CCl ₃ at 93 ppm	CH	CCl ₂	w
	CCl ₃ at 96 ppm	CH	CHCl	w
	CCl ₃ at 115 ppm	CCl	CH ₂	w
	CCl ₃ at 111 ppm	CCl	CH ₂	w
CIPECH-4.32	CH ₂ Cl at 30 ppm	CH	CCl ₂	m
	CH ₂ Cl at 53 ppm	CCl	CH ₂	m
	CHCl ₂ at 63 ppm	CH	CHCl	w
	CHCl ₂ at 68 ppm	CCl	CCl ₂	w
	CHCl ₂ at 74 ppm	CCl	CHCl	w
	CCl ₃ at 95 ppm	CH	CCl ₂	w
	CCl ₃ at 98 ppm	CH	CHCl	w
	CCl ₃ at 105 ppm	CCl	CHCl	w
	CCl ₃ at 111 ppm	CCl	CH ₂	w

^a Relative intensities of absorption peaks: w = weak; m = moderate; s = strong.

gram of the polymer times 10⁴) of the daughter polymers was expected to be the same as that of the parent polymer (PECH). However, this ratio increased about 15 times in the daughter polymers (Table III), indicating that a large excess of initially present double bonds was chlorinated. The number-average molecular weights of the polymers measured by cryoscopy (M_{nCr}) and end-group analysis (M_{neg}) were comparable to those expected if no degradation occurred (M_{nXCr} and M_{nXeg} , respectively). These expected values were calculated on the assumption that no degradation during the chlorination and azidification steps took place, and so the increase in the molar mass of PECH was only due to the substitution of chlorine atoms or azide groups. However, values of F_{OH} higher than its expected value (F_{XOH}) and values of M_{nXeg} higher than M_{neg} indicated the presence of some degradation process.

As the chlorine content increased, initially oily and brown polymers became white and opaque glasses, and their solubility in hydrocarbons, ethers, and chlorinated solvents drastically decreased; therefore, CIPECH-4.32 (Table I) was only soluble in DMSO.

The azidification of these polymers yielded oily products that were yellow to dark brown. The color of the products became darker as the azide content increased. The chlorine contents of AZP-3.83 and AZP-4.32 were 0.15 and 0.04%, respectively. This shows that, despite the presence of chlorine atoms on the tertiary carbon atom (Table II), the substitution of chlorine atoms with azide groups could be achieved with 99.8–99.9% efficiency. In the ¹³C-NMR spectra of AZPs, the absorptions due to chlorine-bearing carbon atoms were missing. In low-azide-content products (AZP-1.16 and AZP-1.64), absorptions due to azidomethyl groups at 52 ppm, besides a variety of absorption peaks appearing between 40 and 70 ppm, were observed. As the azide content of the products increased, the peak at 52 ppm vanished at the expense of others, and this indicated the formation of neighbors of carbon atoms with monoazido, diazido, or triazido groups.

GAP and AZP-0.79 were soluble in almost any organic solvent (dioxane, tetrahydrofuran, acetone, acetonitrile, carbon tetrachloride, and benzene) but were scarcely soluble in water. However, as the polymers

TABLE III
 F_{OH} and F_{DB} Values of PECH and Its Daughter Polymers

Sample	F_{OH}	F_{DB}	F_{OH}/F_{DB}	F_{XOH}	M_{nCr}	M_{neg}	M_{nXCr}	M_{nXeg}
PECH	6.77	0.895	7.56	—	2872	2610	—	—
CIPECH-2.50	5.14	0.048	107.1	4.33	—	3853	—	4069
CIPECH-4.42	3.84	0.032	120.0	2.97	6279	5165	6525	5937
AZPECH-4.42	3.37	0.032	105.3	2.62	7700	5879	7415	6745

TABLE IV
Enthalpies of Combustion (ΔH_c) and Formation (ΔH_f) of AZPs and Cured AZPs

Sample	ΔH_c (kJ/mol ru)	ΔH_c (kJ/kg)	ΔH_f (kJ/mol ru) ^a	$\Delta H_f/N_3$ (kJ/mol) ^b
GAP	-2011	-20,310	116 ^c	—
GAP ^d	-1998	-20,178	103	—
AZP-1.16	-2221	-21,035	349	Reference
AZP-1.64	-2957	-23,604	1153	1675
AZP-3.18	-3360	-17,830	1776	706
AZP-3.50	-3907	-19,383	2369	863
AZP-3.83	-6195	-28,800	4704	1631
AZP-4.32	-7704	-32,754	6283	1878
AZP-4.42	-8335	-34,829	6929	2018
AZP-4.42; cured-0.9	-8452	-35,333	—	—
AZP-4.42; cured-1.0	-8281	-34,618	—	—
AZP-4.42; cured-1.1	-8294	-34,673	—	—

ru = repeat unit.

^a O₂ (g) and combustion products [CO₂ (g) and N₂ (g)] were assumed to be ideal gasses.

^b Molar contribution of azide groups onto ΔH_f of AZPs.

^c Literature value.⁷

^d GAP synthesized in this work.

became richer in azide, their solubility in organic solvents decreased, but they became more soluble in water and DMSO. AZP-3.83 and 4.32 were not soluble in any organic solvent but were very soluble in water and DMSO.

The molar contributions of azide groups to the enthalpy of formation of simple organic compounds were reported to be about 360 kJ/mol.³ We tentatively estimated the molar contribution of azide groups by taking AZP-1.16 as a reference compound (Table IV). The estimated values of this work are much higher than those of the literature (2–5 times higher). We can explain this discrepancy by the assumption that the successive substitution of azide groups on a single carbon atom resulted in extra instability. This explanation also accounts for the large difference between the enthalpies of formation for classical GAP and AZP-1.16. Although the azide contents of these two polymers were almost the same, AZP-1.16 contained azide-rich carbon atoms.

DSC thermograms showed that the glass-transition temperature of GAP was -49.6°C, whereas the glass-transition temperatures of AZPs decreased slightly from -50.5 (AZP-1.16) to -54.5°C (AZP-3.18). However, the decomposition characteristics of GAP and AZPs were quite different. The exothermic decomposition peak of GAP was quite narrow, and it set off at 220°C and finished at 245°C. The decomposition of AZPs started at about 140°C and continued to approximately 280°C, exhibiting a rather broad exothermic peak. Around 400–450°C, another exothermic peak (which might be the continuation of the primary peak) with a higher intensity appeared. In this secondary decomposition stage, decomposition gases evolved so rigorously that the cover of the sample compartment was blown out; therefore, no thermodynamic estima-

tion of the decomposition of AZPs could be performed.

AZP-4.42 was crosslinked into a brown, transparent, and soft rubber with a density of 1.44 g/cm³ (the density of classical GAP is 1.30³, and that of HTTP is 0.93 g/cm³). With a commercial triisocyanate at different CNO/OH molar ratios, the curing of AZP-4.42 was carried out. These products are denoted AZP-Cured: X, where X is the molar ratio of CNO to OH.

As the curing ratio increased from 0.9 to 1.2 mol/mol, the swelling percentage in water and water-extractable components decreased, but mechanical properties, such as the ultimate tensile strength, improved progressively (Table V). The thermal decomposition of cured AZPs was almost the same, starting very slowly just above 50°C, possibly because of absorbed water, and accelerating around 150°C, in agreement with DSC results. At 150°C, AZP-Cured:1.2 lost 8% of its initial mass. Between 150 and 350%, about 40% of the

TABLE V
Physical and Mechanical Properties of Cured AZPs

Sample	EB (%)	EY (%)	YS (μ Pa)	US (μ Pa)	EX (%)	SW (%)
AZP-cured:0.9	159	6.6	0.47	1.40	4.5	14.0
AZP-cured:1.0	125	5.2	1.43	3.41	3.5	12.4
AZP-cured:1.1	124	5.3	1.84	4.23	3.0	12.1
AZP-cured:1.2	124	4.5	2.01	4.84	2.7	10.2
GAP-cured:0.9 ^a	180	—	—	0.32	—	—
GAP-cured:1.0 ^a	230	—	—	0.24	—	—
GAP-cured:1.1 ^a	160	—	—	0.38	—	—
GAP-cured:1.2 ^a	170	—	—	0.42	—	—

EB = elongation at break; EY = elongation at yield; YS = yield strength; US = ultimate tensile strength; EX = extractable fraction; SW = swelling.

^a Literature values.⁸

initial mass was lost. At 160°C, as expected from DSC results, a second stage of acceleration was set off, and decomposition progressed steadily to higher temperatures. At 400°C, about 24% of the sample remained undecomposed.

CONCLUSIONS

AZPs can be synthesized and purified conveniently and easily. They have higher enthalpies of formation than classical GAP, which progressively increase as the azide content increases. In this work, the maximum azide content was 4.42 N₃/repeat unit. However, mass spectrophotometry and ¹³C-NMR studies showed that this value could be theoretically raised to 6.0. AZPs also have low glass-transition temperatures, as sought from a propellant binder, and they form

high-density rubbers on curing. However, the thermal stability of AZPs and cured AZPs must be improved. Some further work on this is in progress in our laboratory.

References

1. Steiner, E. C.; Pelletier, R. R.; Trucks, R. O. *J Am Chem Soc* 1964, 86, 4678.
2. Dixon, J. P. In *Modern Methods in Organic Microanalysis*; Chalmers, R. A., Ed.; Van Nostrand: London, 1968; Chapter 2.
3. Frankel, M. B.; Flanagan, J. E. U.S. Pat. 4,268,450 (1981).
4. Crompton, T. R. *Practical Polymer Analysis*; Plenum: New York, 1993; Chapter 9.
5. Hacaloğlu, J.; Uyar, T. Personal communication.
6. Ewig, D. E. *Org Magn Reson* 1979, 12, 499.
7. Frankel, M. B.; Grant, L. R.; Flanagan, J. E. *J Propul Power* 1992, 8, 560.
8. Bui, V. T.; Ahad, E.; Rheaume, D.; Whitehead, R. *Ind Eng Chem Res* 1997, 36, 2219.