Synthesis of Energetic Polyethers from Halogenated Precursors

Ugo Barbieri,[1] *Giovanni Polacco,**[1] *Roberto Massimi*[2]

Summary: In the solid rocket propellant formulations an important component is the polymeric binder. Actually, the most used binder is hydroxyl-terminated polybutadiene. However, the research is oriented toward the use of energetic polymers which, in addition to the binder function, should improve the propulsion capability of the propellant. In this respect, good candidates are oxetanic polyethers with azidic functionalities in their side chains. Considering the explosive character of such materials, their synthesis must be designed with attention to the safety of the process. In this note, the preparation of azidic copolymers is described and different synthetic strategies are discussed and compared.

Keywords: azido groups; cationic polymerization; energetic polymers; polyethers; solid rocket propellants

Introduction

In the last twenty years, azido polymers have gained interest in the field of energetic binders for solid rocket propellants. For such application, a polymer should possess the following properties: amorphous character and low glass transition temperature ($<-30\,^{\circ}C$), presence of hydroxylic end groups (to allow the formation of a polyurethanic network after *in situ* curing with isocyanates), controlled molecular weight, and low final polydispersity. The basic idea is to substitute the actually used polybutadiene with something that could act not only as a binder but also as a real propellant component. In this respect, a valid solution is the insertion of azido groups due to their tendency to exothermally decompose with nitrogen evolution. There are two possible synthetic strategies for the preparation of energetic azido polymers: i) homo or copolymerization of etheric monomers containing the azido group in the side chains; ii) synthesis of a polyether with suitable leaving groups (i.e. halogen atoms) in the side chain and subsequent introduction of the azido groups by nucleophilic substitution. The following scheme represents the two strategies for an oxetanic monomer carrying two leaving X groups.

The main restriction of the first synthetic route is related to safety, because it involves the handling and storage of monomers which are considerably more unstable and shock-sensitive than the corresponding polymers. Therefore, from this point of view the second route is highly preferable and has been used, for example, for the preparation of glycidyl azide polymer (GAP) from poly-epichlorohydrin (pECH) by nucleophilic displacement of chlorine atoms.[1] However, this solution is not always possible because, from a kinetic point of view, the substitution of the leaving groups from the polymer is often more difficult than from the monomer.

In the present work, we describe the preparation, by the second synthetic route, of energetic *co*-polyethers containing oxetanic repeating units. Among oxetanic polymers, poly-3,3-bis (azidomethyl) oxetane (pBAMO) is rather interesting, due to its high N-content (50% w, while GAP has

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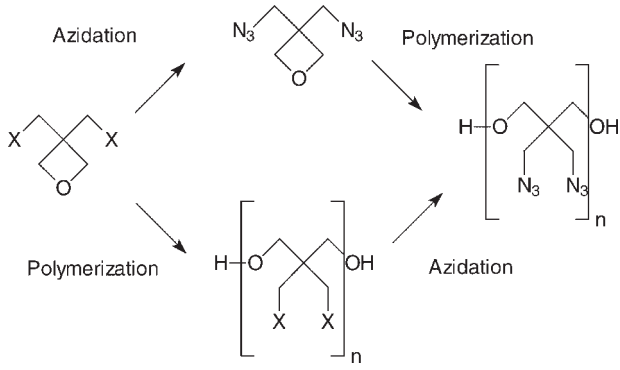
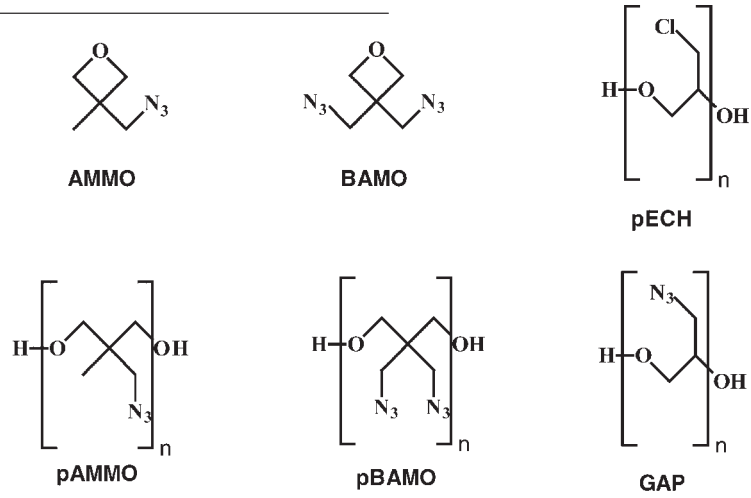


only 42%). Unfortunately, pBAMO cannot be used as a homopolymer in binder formulations, due to its high crystallinity; therefore, it is necessary to break up its chain regularity by the random introduction of other monomeric units along the chain. In this way, the energetic content of pBAMO is partially sacrificed in favor of processability. In other words, a *co*-monomer must be added in the minimum quantity necessary to induce amorphous properties to the material. In this respect, good candidates can be 3-azidomethyl-3-methyl oxetane (AMMO) or the glycidyl azido (GA) unit. Amorphous copolymers BAMO/GA have been prepared by azidation of poly(3,3-bis (chloromethyl)oxetane-*co*-epichlorohydrin) (BClMO/ECH) and poly(3,3-bis (bromo-methyl)oxetane-*co*-epichlorohydrin) (BBrMO/ECH). In addition, azidation was performed on pClMMO and pBBrMO in order to synthesize pAMMO and pBAMO, respectively.

The structure formulas of AMMO, BAMO, pECH, pAMMO, pBAMO and GAP are reported in the following scheme. The other formulas of non-azidated monomers and polymers can be derived by substitution of the azidic functional group with the appropriate halogen atom.



Experimental

Monomers Synthesis

ClMMO was synthesized with purity over 99%, (determined by gas chromatography (GC)) from 3-hydroxymethyl-3-methyl oxetane (HMMO), using CCl_4 and triphenylphosphine as chlorinating medium,

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according to a procedure described in literature.[2] BClMO was synthesized starting from pentaerythritol by substitution of three out of the four hydroxyl groups with chlorine atoms and subsequent formation of the oxetanic ring by NaOH in ethanol.[3,4] The same procedure was used for the formation of oxetanic ring from bis-bromomethyl-3-bromo-propan-1-ol, kindly provided by ICT Fraunhofer, to obtain BBrMO with 97% purity. AMMO was prepared from ClMMO using NaN_3 and dimethylformamide (DMF);[5] BAMO was prepared from BBrMO in aqueous solution using NaN_3, NaOH and tetrabutylammonium bromide (TBAB) as phase transfer catalyst.[6] In both cases a quantitative substitution of the halogen atom with the azidic group was obtained. All the above-mentioned monomers were stored at 4 °C, in the absence of light in order to avoid the formation of peroxides.

Polymerization Procedure

The polymerization of AMMO and BAMO was run in methylene chloride solution, using triethyloxonium hexafluorophosphate and 1,4-butanediol (1/1) by the procedure suggested by Wardle.[7] The copolymers BClMO/ECH and BBrMO/ECH were prepared in condition analogous to those described for pAMMO and pBAMO, even if some tests were run using different catalyst/initiator systems (see Table 2). The azidic monomers and homopolymers were characterized according to procedures STANAG 4487 and 4489 in order to evaluate their sensitivity to friction and impact, respectively. Thermal properties were determined by differential scanning calorimetry using a TA Q500 apparatus (scanning rate of 10 °C/min). The molecular weights reported in the table were measured at room temperature with a gel permeation chromatography (GPC) apparatus Jasco PU-1580, equipped with PL Mesopore column, using polystyrene standards.

Copolymers Azidation Procedure

The azidations of the copolymers were run using NaN_3 and DMF as solvent at 90–95 °C. After cooling to room temperature, distilled water was added in order to allow the separation of the polymer, which was washed, dried and finally purified by dissolution in acetone and re-precipitation in methanol. The substitution of the halogen atoms by azidic groups was followed by FT-IR on a Bruker Tensor 27 and ^{1}H-NMR on a VXR300 instrument and, for copolymers BBrMO/ECH, by ^{13}C-NMR on VXR300. ^{1}H-NMR and ^{13}C-NMR spectra were recorded in solution of DMSO-d_6 or $CDCl_3$ at room temperature.

Results and Discussion

AMMO and BAMO Monomers and Homopolymers

The polymerization of oxetanes is usually carried out by living cationic polymerization using an adduct of the pre-initiator precursor and a catalyst.[8,9] However, the presence of azido groups in the cyclic monomer may significantly reduce the polymerization rate; therefore, extremely long reaction times may be needed and the obtained polymers may have very low molecular weights. Recently, different catalytic systems, such as, e.g., a combination of an alkylating salt (triethyloxonium hexafluorophosphate (TEOFF)) as catalyst and a selected alcohol as precursor[7] were shown to overcome these limitations.

The results (Table 1) showed that, at atmospheric pressure, AMMO and BAMO evaporate before thermal decomposition starts; however, they result highly unstable to mechanical shocks if compared with the corresponding homopolymers. The main reason is probably that the four member oxetanic ring is highly stressed and this lowers considerably the energetic activation threshold under mechanical stress.

Copolymers Synthesis

From the results reported in Table 1, it is clear how the safety limits of a synthetic process would be larger running the azidation on preformed polymers having suitable leaving groups in side chains. In this case, a

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Table 1.
Comparison between sensitiveness properties of azido compounds.

Sample	Polymers		Monomers	
	pAMMO	pBAMO	AMMO	BAMO
Decomposition Temperature (°C)	244	258	Not observed	Not observed
Impact Test (J)	Explosion not observed	Explosion not observed	19.6	0.49
Friction Test (Kg)	36	36	6	4

low azidation kinetic is expected, however this disadvantage should be overcome by the advantage of handling safer compounds. Therefore, the polymerization/azidation route, even if not preferable at lab-scale, has to be considered as the preferable one having in mind the scale up of the process. Nevertheless, this solution has been poorly studied in the past.

To our knowledge, with the exception of GAP synthesis, the only substitution of chlorine atoms with azido groups in polymers has been reported by Proud'-Homme[10] in copolymers BClMO/ε-caprolactone (ε-CL), with reaction time ranging from 1 to 20 days depending on the percentage of ε-CL units. In all tests (Table 2), the initial monomeric molar ratio was equal to one ($[BXMO]_0 = [ECH]_0$, where X=Cl, Br).

The FT-IR spectra of copolymers "A" and "2" (Table 2) are reported in Figure 1; the bands at 745 and 696 cm^{-1} are due to the C–Cl stretching of ECH and BClMO units respectively, while the presence of bromine atoms is revealed by the peak at 607 cm^{-1}. The exact composition of the copolymer BClMO/ECH was determined by ^{1}H-NMR spectroscopy, which showed a peak at 3.47 ppm that was assigned to methylenic protons of BClMO nearby the oxygen atoms in the main chain. Unfortunately, the same procedure is not possible with the copolymer BBrMO/ECH because in the ^{1}H-NMR spectrum the peaks resulted superposed.

Therefore, a quantitative measurement was performed by ^{13}C-NMR analysis (Figure 2). In this way, the peaks of CH_2Br and CH_2Cl resulted at 36.0 and 44.7 ppm, respectively. Even if the latter peak is overlapped with that of quaternary carbon of BBrMO, it is possible to determine the composition of the copolymer by integra-

Table 2.
Copolymerization BXMO/ECH (initial monomeric ratio = 1/1).

	C_{mon}	$C_{initiator}$	$C_{poly\text{-}ol}$	Ratio BDO/I	Polym. time	Y_{ev} [a]	Y_{pr} [b]	Mn [c] GPC	Mw/Mn	BXMO
	mol/L	mol/L	mol/L		h	%	%			%
					BClMO/ECH					
A	0.88	$8.8 \cdot 10^{-3}$ [e]	0.0176 [d]	2	72	37.7	28.9	4164	1.3438	60
B	0.88	0.0176 [e]	0.0176 [d]	1	24	83.9	64.3	3845	1.4875	72
C	0.88	0.0176 [e]	0.0176 [d]	1	72	84.2	58.4	3387	1.4864	67
D	0.88	0.0176 [e]	$8.8 \cdot 10^{-3}$ [d]	0.5	72	89.5	62.5	1922	1.4071	57
					BBrMO/ECH					
2	2.95	0.074 [e]	0.074 [f]	1	72	85.6	46.0	—	—	67
3	2.85	0.074 [g]	0.074 [f]	1	24	52.1	28.7	—	—	71
4	2.95	0.074 [g]	0.11 [d]	1.5	24	72.7	17.2	—	—	—
4g	2.95	0.074 [g]	0.11 [d]	1.5	24	63.3	11.0	—	—	—

[a] Yield referred to copolymer obtained through solvent evaporation.
[b] Yield referred to copolymer purified by precipitation in methanol from CH_2Cl_2 solution.
[c] M_n referred to purified product.
[d] Poly-ol = butanediol (BDO).
[e] Initiator (I) = TEOFF.
[f] Poly-ol = 1,1,1-(trishydroxymethyl) oxetane.
[g] Initiator (I) = boron trifluoride etherate (TFBE).

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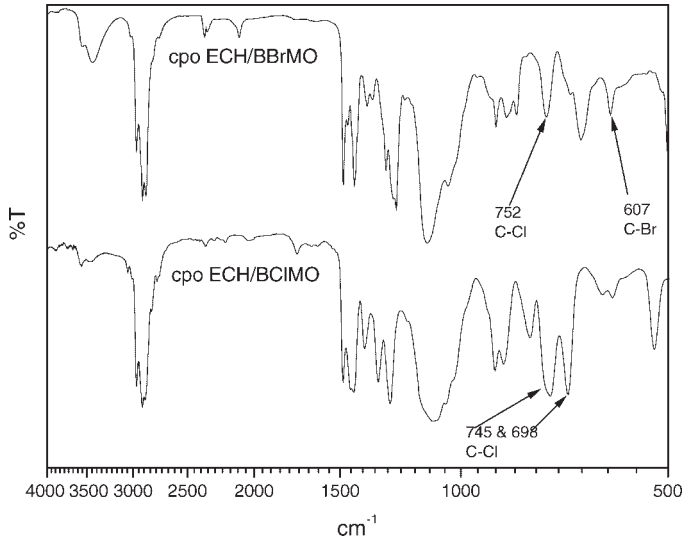

Figure 1.
FT-IR spectrum of BBrMO/ECH, BClMO/ECH copolymers.

tion. This result was confirmed by integration of the two peaks at 71.0 and 69.9 ppm, relative to secondary carbons of the BBrMO and ECH units.

It can be seen from Table 2 that for all copolymerizations, starting from an initial monomer ratio equal to one, copolymers having 60–70% of BXMO units in the chain were obtained. However, it is important to point out that the measured composition depends not only on the initial monomer concentration, but also on the purification process of the copolymer. In fact, the chains with high content of ECH units and low

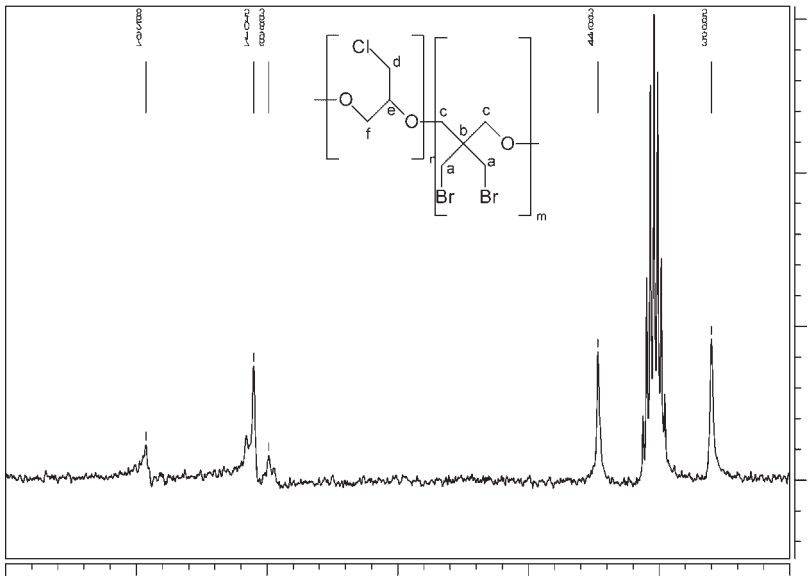

Figure 2.
^{13}C-NMR of copolymer ECH/BBrMO.

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molecular weight can remain in solution during precipitation in methanol. As an example, the copolymer "C" has Mn = 2878 and Mw/Mn = 1.66 before purification; and Mn = 3387 Mw/Mn = 1.48 after purification. Therefore, the purification process implies a "fractionation" of the polymer, leading to a product with higher molecular weight and lower ECH content.

Azidation of Copolymers

The substitution reaction of N_3 is a SN2 type with contemporary formation and breakage of molecular bonds. In spite of its moderate nucleophilic character, N_3 allows the substitution of halogen atoms on 3-halomethyl substituted oxetanes (whose structure are similar to those of a neopentylic halide, kinetically slow in SN2 reactions) with good yield and reasonably short reaction time. This behaviour has been explained hypothesizing that the oxetanic ring binds the halomethylenic groups and assumes a less hindered position, favorable for nucleophilic substitution.[11] Considering the good results obtained for the azidation of pECH in DMF, we tried the same procedure on random BClMO/ECH copolymers, in order to investigate if the azido groups are able to substitute chlorine atoms on opened ring oxetanic units. Unfortunately, it was not possible to test the azidation directly on pBClMO because of its high crystallinity which limits the solubility in most common aprotic and polar solvents (like DMF or DMSO) used in nucleophilic substitution reactions.

The quantification of energetic groups by ^{1}H-NMR analysis was not possible due to peak overlapping; therefore, the percentage of azido groups was determined semi-quantitatively by FT-IR analysis, following the growth of the characteristic absorption of N_3 group (2100 cm^{-1}) and the decrease of the intensity of C–Cl peaks (700–745 cm^{-1}) during the course of reaction (Table 3). From the data reported in Table 3 it can be seen that complete azidation of the copolymeric substrate wasn't achieved even with the use of a considerable excess of NaN_3.

Table 3.
Azidation test on BClMO/ECH copolymers of different compositions.

Copolymer composition	NaN_3 excess	Reaction time	Percentage of introduced azido groups
% BClMO	%	h	%
60	15	3	35
67	15	24	55
67	45	24	65
67	100	24	60
67	15	29	70
67	15	34	75
72	15	24, 48, 120	60, 65, 85

In conclusion, the introduction of BClMO units, among the ECH ones, slows down the reaction rate of azidation. In fact, while ECH has only a chloromethylenic group in each monomeric unit, BClMO has two CH_2Cl on the same quaternary carbon atom and this enhances the steric hindrance of the oxetanic units. Moreover, the azido groups are polar and weakly electron-accepting, therefore, during azidation they can interact with the chlorine bonded to a $–CH_2$ of the same monomeric unit. This would decrease the –Cl mobility and, as a consequence, its ability to leave the polymeric substrate. However, it is important to underline that the incomplete substitution of Cl doesn't impair the energetic properties of the copolymers, which abruptly decompose around 227 °C.

Anyhow, this incomplete substitution is the reason why we replaced the oxetanic chlorine with bromine atoms, which should have a higher tendency to leave the polymeric substrate thanks to their greater molecular radius. The azidation was performed in DMF, at 95 °C, using a 20% excess of NaN_3 and, for the copolymer BbrMO/ECH = 33/67, a complete substitution was obtained after 96 h of reaction. From Figure 3 it can be seen that after azidation the bands characteristic of the C–N_3 group (2530 cm^{-1} $2\nu_s(N_3)$, 2100 cm^{-1} $\nu_{as}(N_3)$, 1290 $\nu_s(N_3)$, 553 cm^{-1} N_3 bend[12]) are present, while the bands corresponding to C–Br (605 cm^{-1}) and

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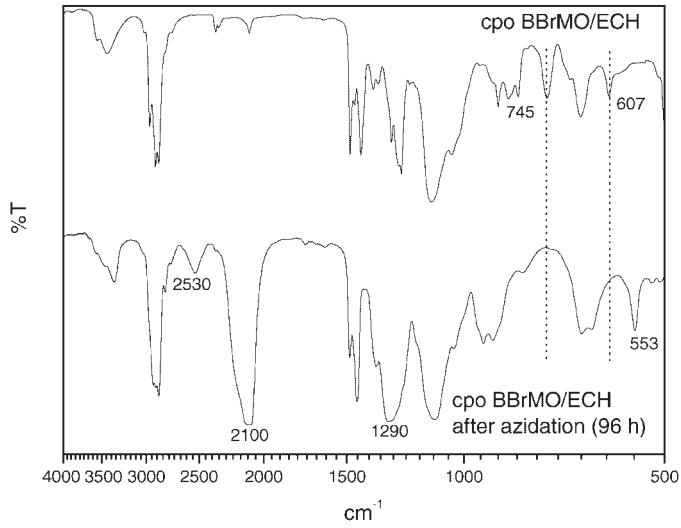

Figure 3.
Comparison between FT-IR spectra of BBrMO/ECH copolymer before and after azidation.

C–Cl (752 cm^{-1}) bonds completely disappear. The complete substitution is confirmed comparing the ^{13}C-NMR spectra obtained before (Figure 2) and after azidation (Figure 4). In the latter, a new peak, corresponding to the secondary carbons of the side chain bonded to N_3 group, appears at 52.03 ppm, while no evidence of CH_2Br (around 35–36 ppm) is present.

As expected, the obtained azido copolymer (Mn = 6700, Mw/Mn = 2.21, N-content = 48.3%) shows energetic properties, due to the instantaneous decomposition of

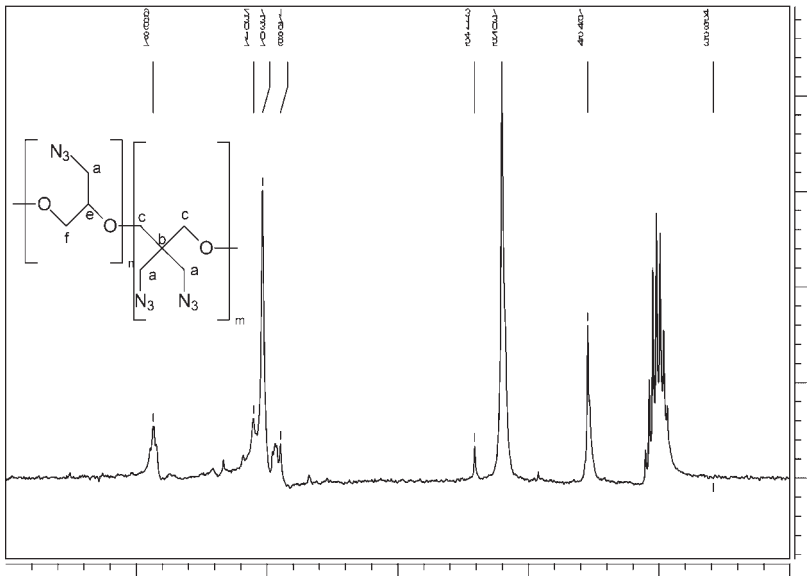

Figure 4.
^{13}C-NMR spectrum of copolymer BBrMO/ECH after azidation (96 h).

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the azido groups around 240 °C, with a relative weight loss of 35.5%, value quite close to that (32.3%) corresponding to the release of a N_2 molecule from each azidic group. If the heating is protracted until 400 °C, no other decomposition peak is observed; however the sample weight loss goes on slowly due to the progressive breakage of the macromolecular chains of the polymer.

Conclusions

Azido copolymers can be prepared either from pre-azidated monomers or by introduction of N_3 functionalities in a preformed copolymer containing suitable exiting groups, like i.e. halogen atoms. The second way is surely preferable in view of the safety of the process. However, from a synthetic point of view, the first way is fast and flexible, while in the second one the reaction rate and the percentage of N_3 groups that can be introduced depend critically on the nature of leaving groups and substrate. As an example, GAP polymers are usually prepared from pECH, while the same procedure is less simple if the chlorine atom is on an oxetanic polymer. In fact, for solid rocket propellant, the presence of the BAMO oxetanic unit would guarantee energetic properties higher than those of GAP. Considering the crystalline nature of pBAMO, a possible solution is the synthesis of a copolymer BAMO-GA where the oxiranic units have to be introduced in order to obtain an amorphous material. In this work it has been shown that starting from p(BclMO/ECH), only a partial substitution of chlorine atoms can be obtained, while BBrMO/ECH copolymers can be successfully azidated, even if with quite long reaction times, thanks to the higher nucleofugacity of bromine. The synthesized copolymer, with BBrMO/ECH ratio equal to 67/33, has a high N-content (48.3% w) which guarantees energetic properties very close to those of pBAMO (n = 50.0% w). Although the azidation step doesn't cause any appreciable degradation of the main chains, it remains to study how it may affect the number of hydroxylic end-groups per macromolecule, which is important for the subsequent cross-linking with isocyanates.

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