Homo- and copolymers of 3-tosyloxymethyl-3-methyl oxetane (TMMO) as precursors to energetic azido polymers

Ugo Barbieri,[1] Thomas Keicher,[2] Giovanni Polacco[1]*

[1*]Department of Chemical Engineering, University of Pisa, Via Diotisalvi 2, 56126 Pisa, Italy; fax: +39 050 2217820; e-mail: g.polacco@ing.unipi.it.
[2]Fraunhofer-Institut für Chemische Technologie (ICT) Postfach 1240, D-76327 Pfinztal, Germany; fax: +49(0)8912057531; e-mail: thomas.keicher@ict.fraunhofer.de.

Abstract: Poly(3-azidomethyl-3-methyloxetane) and its copolymers with 3,3-bis(azidomethyl)oxetane were synthesized by cationic polymerization from 3-tosyloxymethyl-3-methyl oxetane and 3,3-bis(bromomethyl)oxetane, using a polyol as initiator and boron trifluoride complex as catalyst, followed by azidation. The final objective is the synthesis of an energetic binder to be used for rocket propellants and therefore the effects of different initiator/catalyst systems on important properties, like, i.e., the molecular weight distribution and the functionality of the polymer, were investigated. It was found that, even though both the operating conditions and the catalytic system were chosen in order to grant the living character of the polymerization, the latter seems to be prevalently driven by an "active chain end" mechanism. In particular, this may lead to the undesired formation of a small quantity of oligomers and to the presence of non-hydroxylic chain-end functionalities. Nevertheless, the average number of OH groups can be strictly controlled when boron trifluoride tetrahydrofuranate is used as catalyst.

Introduction

In the last twenty years, azide polymers have gained interest in the technology of solid rocket propellants (Gaur et al. [1]); usually, they are low molecular weight polyethers with azide groups in the side chains, capable of improving the specific impulse of the propellant by exothermic decomposition with nitrogen evolution. The research has been mainly focused on poly(3-azidomethyl-3-methyloxetane) (pAMMO) and its random or block copolymers with 3,3-bis(azidomethyl)oxetane (BAMO) and glycidyl azide (GA), as the most promising polymers for "performance-enhanced" binders of solid propellants (Murali Mohan et al [2]).

In the past, such azide polyoxetanes have been synthesized by polymerization of their respective monomers and many catalytic systems have been tested (Cheradame et al [3]). The main limit of this synthetic route is related to safety, as it involves the handling and storage of azide-oxetanes which are considerably more unstable and shock-sensitive than the corresponding polymers. For this reason, we recently synthesized azide polymers, such as pAMMO and the random copolymer p(GA-*co*-BAMO), by direct azidation of their polymeric precursors poly(3-tosyloxymethyl-3-methyl oxetane) (pTMMO) and poly(epichlorohydrin-*co*-3,3-bis(bromomethyl)oxetane) p(ECH-*co*-BBrMO), rather than by polymerization of the azide monomers (Barbieri et al [4], [5]).

Two important features of the polymers to be used as binders are that they must be amorphous and contain a well-defined number of hydroxyl end-groups to allow the formation of a polyurethane network by reaction with isocyanates. This network binds together the redox charge of the propellant, i.e. ammonium perchlorate and aluminum, in an elastomeric rubber whose toughness is directly linked to the crosslink density. The concentration of the hydroxyl end groups can be controlled by optimizing the parameters of the polymerization of the halogenated/tosylated oxetanes (i.e., type and amount of catalyst and co-catalyst, temperature, etc.) and it is not affected by the subsequent azidation.

The cationic polymerization of cyclic ethers is usually carried out in presence of a Lewis acid and a polyol (Penczek et al [6]). Theoretically, the polymer molecular weight and the concentration of OH functionalities are easy to control, if the polymerization proceeds with a living mechanism. The term Activated Monomer Mechanism (AMM) was introduced to describe the living mechanism of propagation of cyclic ethers, which has been already discussed in several papers (Kubisa et al. [7]). Its main feature is that the polyol-initiated polymer chains grow uncharged, thus basically avoiding termination reactions. Under these conditions, the number of OH functionalities in each macromolecule is equal to the number of OH groups of the polyol (e.g., a polymer tri-hydroxy-terminated could be prepared by employing a triol as initiator). Unfortunately, a competition between AMM and Active Chain End (ACE) propagations (Figure 1) is possible, particularly if the instantaneous monomer concentration is not kept much lower than that of the OH groups. Therefore, in order to kinetically hinder the ACE propagation, the polymerization must be carried out feeding the monomers drop by drop during the whole reaction time.
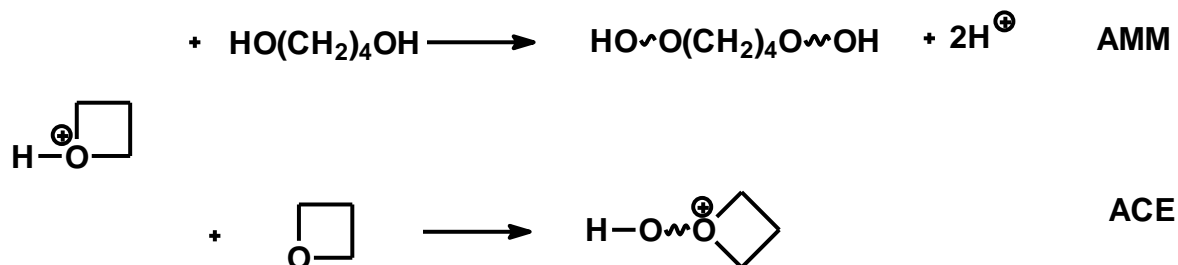

Fig 1. "Living"(AMM) and "not living"(ACE) propagation for an oxetane monomer in the presence of butanediol.

If some of the chains grow by ACE propagation, termination reactions are possible and polymers with lower OH functionalization and lower molecular weight are obtained. Moreover, back-biting reactions are also possible, thus generating cyclic oligomeric structures in addition to the linear chains.

A study of the homopolymerization of TMMO and its copolymerization with BBrMO has been carried out by using several initiator/catalyst systems, in order to obtain polymers with both a well-determined number of OH end functionalities and a limited content of cyclic oligomers. A full characterization of such polymers is presented and the final azidation is performed on the polymeric substrates to obtain the desired pAMMO and p(AMMO-co-BAMO).

Result and discussion

TMMO homopolymerization

In order to assist chain propagation by AMM, the homo-polymerization tests were performed by slowly dropping a TMMO solution (0,022 mol/h) in a batch containing the boron trifluoride etherate (TFBE)/polyol initiating system. Three different polyols (1,4-butanediol (BDO), 1,1,1-tris(hydroxymethyl)ethane (THME) and glycerol (GLO)) and several TFBE/OH ratios were employed to investigate how these parameters affect the concentration of OH end groups and the properties of the final homopolymer. In all tests, an amount of polyol equal to 2 mol% with respect to the monomer was used, so that the molecular weight expected for AMM propagation should be about 11,600. Considering the weight loss due to azidation, the theoretical molecular weight of the final pAMMO should be about 6,000. The operating conditions and the properties of the obtained polymers are reported in Table 1.

Tab. 1. Polymerization tests performed on TMMO (polyol = 2 mol% with respect to the monomer).

pTMMO n-polyol	OH/TFBE	Yield (%)	M_n (GPC) 11600 (calc.)	OH eq.weight	N_{OH} per chain titration	N_{OH} per chain ^{1}H-NMR	Oligomers (wt%)	M_w/M_n
1-BDO	1	88.1	7,574	5,089	1.48	1.08	0.2	1.91
2-BDO	2	92.0	6,890	5,089	1.35	1.45	0.3	1.79
3-BDO	4	90.9	6,492	4,348	1.49	1.28	0.3	1.75
1-GLO	0.5	92.4	3,687	-	-	1.22	2.4	1.62
2-GLO	1	90.7	4,467	-	-	1.27	1.7	1.71
3-GLO	3	93.7	5,267	3,945	1.33	1.21	1.0	1.83
1-THME	1	82.0	4,196	3,401	1.23	1.30	2.0	1.62
2-THME	3	94.4	5,304	3,545	1.49	1.47	1.1	1.62

In all the polymerizations, the total yield in pTMMO was around 90% and did not seem to be affected by the type of polyol employed nor by the OH/TFBE ratio. In all cases, the GPC analyses (Figure 2) pointed out the presence of a small amount of oligomers with both number- and weight-average molecular weights close to 800, thus corresponding mainly to trimers. When BDO was employed as co-catalyst the smallest, almost negligible, (0.2-0.3 wt%) quantity of oligomers was formed.

However, besides the small quantity of oligomers formed in most polymerizations, no further indication pointing to an AMM mechanism was provided by the GPC analysis. In fact, regardless of the polyol and the OH/TFBE ratio used, the polymer molecular weight was always lower than expected and the M_w/M_n ratio was too high for a "living" polymerization. Moreover, the number of hydroxyl functionalities did not change if a triol or a diol was used as co-catalyst. From this point of view, more important information came from the NMR analysis, which showed that in none of the polymerizations the alcohols acted as initiators. As an example, Figure 3 shows that in the ^{1}H-NMR spectra of pTMMO1-BDO there are no peaks in the 1.7-1.4 ppm region, where the signal from O-CH2-CH2-CH2-CH2-O should appear. The same was found for samples of pTMMO prepared by using THME or GLO as co-catalysts. The absence of initiator units in the polymer chains means that the latter do not grow

3

through the expected AMM. It is not surprising, therefore, that the theoretical number of OH per macromolecule was always lower than two and did not increase when a triol, rather than a diol, was used as co-catalyst.
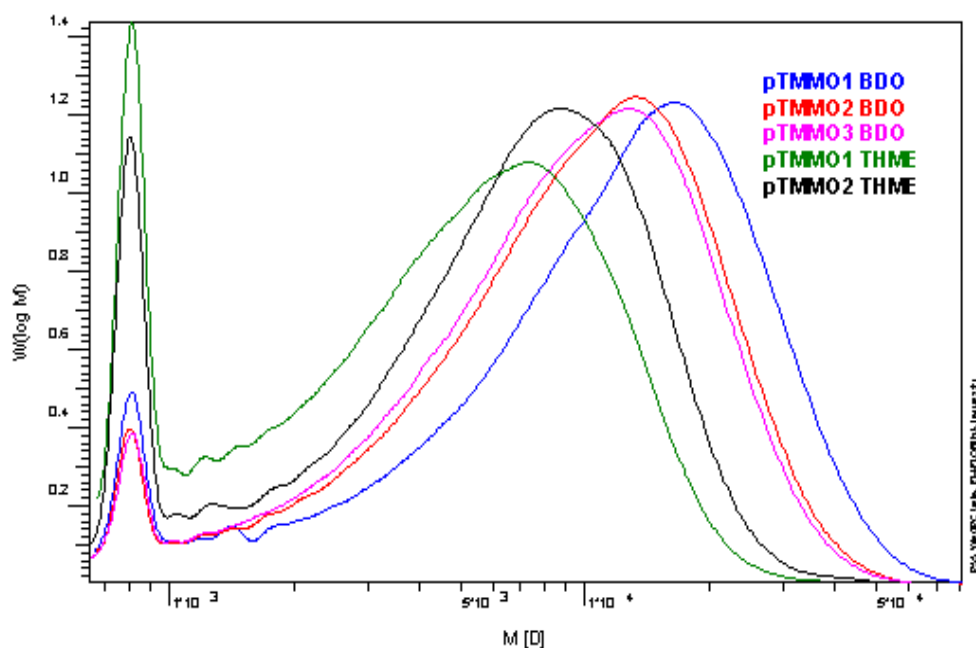

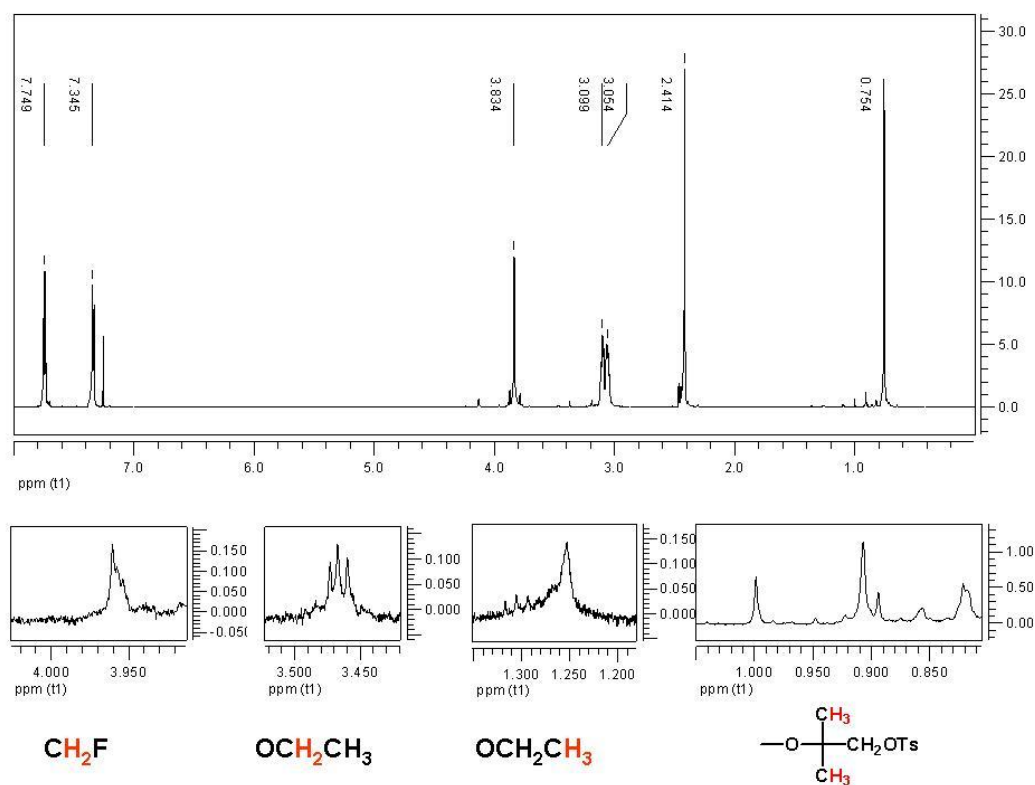**Fig. 2.** GPC analysis of some pTMMO samples.

Fig. 3. ^{1}H-NMR spectra of pTMMO1-BDO. δ (ppm): 7.75-7.34 ppm (aromatic protons of Ts), 4.15-4.13 (end OH(acetylated)- TMMO), 3.83 (CH_2OTs), 3.10 (CH_2O-TMMO), 2.41 (arylic CH_3- TMMO), 0.75 (CH_3-TMMO).

4

In conclusion, whatever is the employed polyol, the chain propagation does prevalently occur by the ACE mechanism and termination reactions may lead to end-groups without OH functionalities. As an example, the ^{1}H-NMR spectra (Figure 3) show a peak at 0.91 ppm which can be assigned to aliphatic end groups coming from the TMMO monomer. Moreover, other termination reactions probably involve the decomposition of TFBE as suggested by the presence of the peaks at 4.13 ppm and 3.37-1.25 ppm, ascribable to terminal CH_2F and OCH_2CH_3, respectively. An investigation of the exact mechanism of these termination reactions, which is still obscure, was beyond the scope of this study. Probably, the only reason why the contribution of back-biting reaction is negligible is the high steric hindrance of TMMO.

TMMO/BBrMO copolymerization

The co-polymerization tests were performed through the same procedure used for TMMO homopolymerization. The amount of polyol was equal to 2 mol%, with respect to the monomer and the mixture TMMO/BBrMO=75/25 (mol) was fed at rate of 0.018 mol/h into the batch containing the initiating system.

Tab. 2. Copolymerization tests from monomeric mixture TMMO/BBrMO 75/25 (polyol=2% mol with respect to the monomer).

Copolymer n-polyol	OH/TFBE complex	Yield (%)	M_n (GPC)	OH eq. weight	N_{OH} for chain		Olig (%w)	M_w/M_n	%BBrMO
			12,810 (calc.)		Titr.	^{1}H-NMR			
1-BDO	1	90.1	6,472	7,967	0.81	0.78	0.6	1.92	23.7
2-BDO	1	89.5	5,803	-	-	1.27	0.8	1.96	25.2
3-BDO	2	85.3	4,951	3,822	1.29	0.75	0.9	1.77	27.5
4-BDO	4	90.4	4,356	2,518	1.73	1.51	1.2	1.68	24.3
5-BDO[1]	1	82.7	5,583	-	-	2.11	0.8	1.87	26.7
1-THME	1	92.6	3,908	4,799	0.81	1.15	2.8	1.82	25.9
2-THME[2]	1	88.7	3,963	-	-	1.50	2.5	1.77	26.6
3-THME[1,2]	1	88.4	6,472	-	-	3.46	2.5	1.74	26.7

(1): Boron trifluoride tetrahydrofuranate (TFBTHF) as catalyst
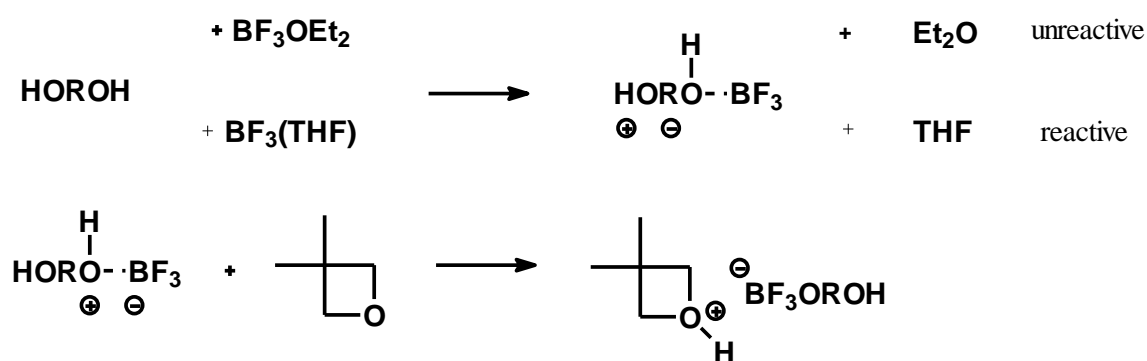(2): 1,2-dichloroethane as solvent

Fig. 4. Initiation of the polymerization.

The comonomers ratio was chosen as a good compromise between the energetic and morphological properties of the expected copolymer. In fact, a greater amount of BBrMO would increase (after azidation) the N-content of the energetic polymer but also its cristallinity, thus reducing the elastomeric character of the final polyurethane network. The composition of the copolymer was always found to respect such ratio.

For all the polymerizations where TFBE was used as catalyst, the number of OH groups per chain and the amount of cyclic oligomers (Table 2) were found to be quite similar to those measured for the homopolymers thus showing that the presence of BBrMO does not affect the reaction mechanism, which is still prevalently under ACE conditions. In fact, in these cases the previous discussion about the homopolymerization of TMMO can be extended to the copolymer.
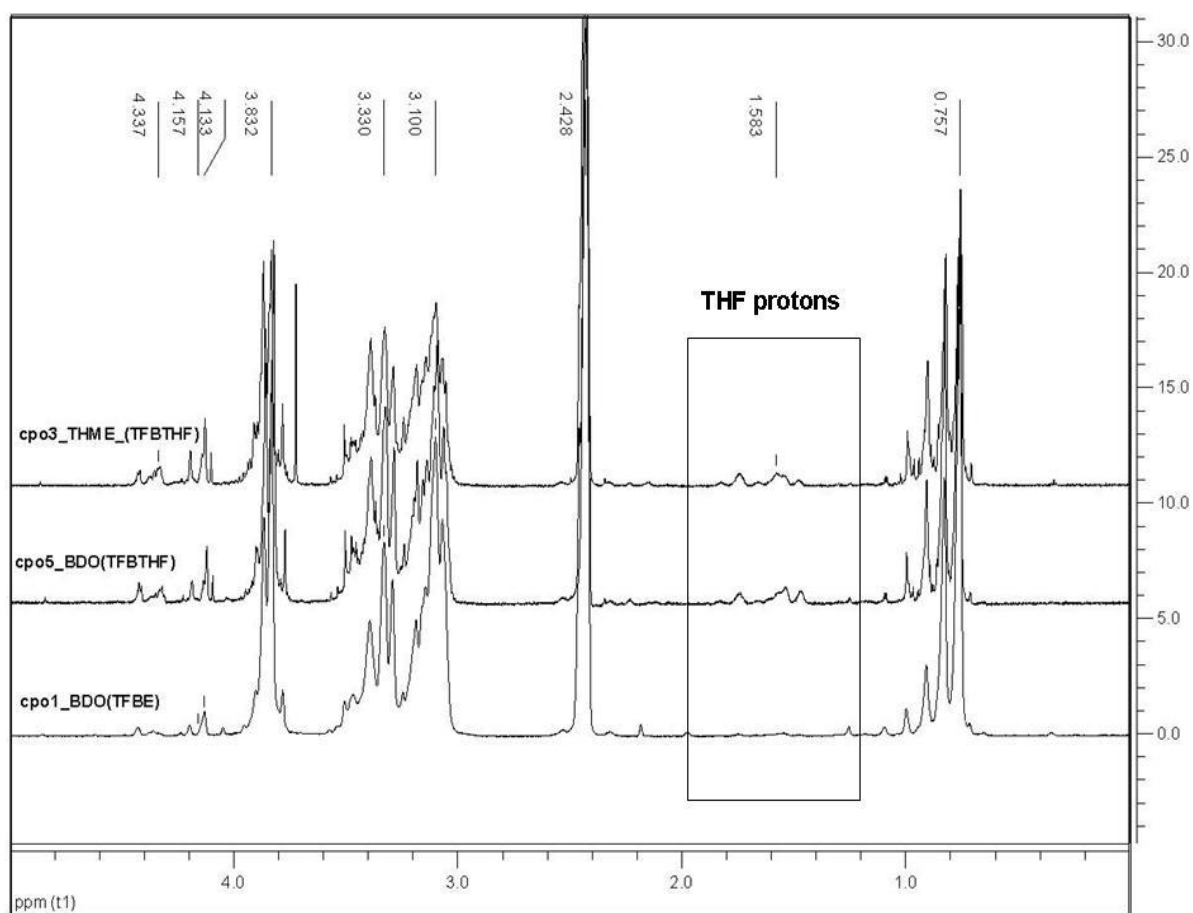

Fig. 5. ^{1}H-NMR spectra of TMMO-co-BBrMO: δ (ppm) 4.34 (end OH(acetylated)-BBrMO),4.15-4.13 (end OH(acetylated)- TMMO), 3.83 (CH$_2$OTs), 3.33(CH$_2$-BBrMO), 3.10 (CH$_2$O-TMMO), 2.43 (arylic CH$_3$- TMMO), 1.58 (CH$_2$-THF), 0.76 (CH$_3$-TMMO).

On the other side, the number of OH functionalities was found to be strongly dependent on the polyol when boron trifluoride tetrahydrofuranate (TFBTHF) was used as catalyst. In this case, a di-hydroxyl terminated TMMO-*co*-BBrMO was synthesized (Table 2, test 5/BDO) and even more than three OH end groups per chain were calculated (Table 2, test 3/THME) by using, respectively, a diol or a triol as initiator. Moreover, both the ^{1}H-NMR spectra of copolymers (Figure 5) synthesized through TFBTHF indicated the presence of some THF units in the polymer chains,

Unauthenticated
Download Date | 7/30/18 4:39 AM

independently from the used polyol, thus showing that the kind of TFB-complex is important in determining the polymerization mechanism. In fact, when TFBE is employed, the ether does not enter the polymer chains and the initiation mechanism is thought to be that shown in Figure 4.

On the other side, it seems reasonable to expect THF to behave like an oxetane, during chain propagation, thus entering the polymer chains. Nevertheless, even if TFBTHF allows the formation of co-polymers with a well-determined number of OH end groups, the ACE mechanism is still present and both molecular weight and polydispersity will differ from those expected when AMM prevails. Actually, the role of the polyol in chain propagation and its interaction with TFBTHF are not clear, yet. Moreover, it should be underlined that detecting the polyols in the co-polymer backbone by ^{1}H-NMR is not easy because of peaks overlapping.

Azidation of the polymers

The conditions and the kinetics of the azidation of pTMMO were deeply investigated and reported in a previous paper [5]. Analogously to pAMMO, the copolymer p(AMMO-*co*-BAMO) was obtained by displacement of bromine and tosyloxy groups by azide groups. The polymers were characterized by ^{1}H-NMR and FT-IR ad their properties are summarized in Table 3.

Tab. 3. Properties of the azide polymers and their precursors.

polymer	% BXMO	Mn	Mw/Mn	OH/chain	%oligomer	% azide
pTMMO	-	5,718	1.87	1.29	1.0	-
pAMMO	-	3,776	2.09	1.34	1.2	98.6
TMMO-co-BBrMO	25.8	5,188	1.82	1.56	0.9	-
AMMO-co-BAMO	25.5	4,243	2.17	1.58	0.7	97.9

The displacement of leaving groups was checked by FT-IR (disappearance of the bands at 1,356 cm^{-1}, 1,179 cm^{-1} and 846 cm^{-1}, corresponding to OTs, and 605 cm^{-1}, corresponding to C-Br, and appearance of two bands at 2,100 cm^{-1} and 1,283 cm^{-1}, corresponding to asymmetrical and symmetrical N$_3$ stretching, respectively) and was confirmed by ^{1}H-NMR (Figure 6 shows peaks at 3.285, 3.234 ppm (CH$_2$O and CH$_2$N$_3$) and 0.969 (CH$_3$), characteristic of pAMMO). As expected, the azidation was quantitative for both polymers; the percentage displacement of tosyl by azide groups being 98.6% and 97.9%, respectively, for the homo- and the copolymer.

As expected, the azidation does not change significantly the properties of the polymers in terms of OH equivalent/macromolecule, amount of oligomers and molar composition (for the copolymer). However, it is interesting to note that the molecular weight and the polydispersity of the azide polymers are both higher than expected from the parent polymers. This may be explained by assuming that chain-extension may occur, at least in part, as a secondary reaction, probably due to the high temperature conditions of the azidation.
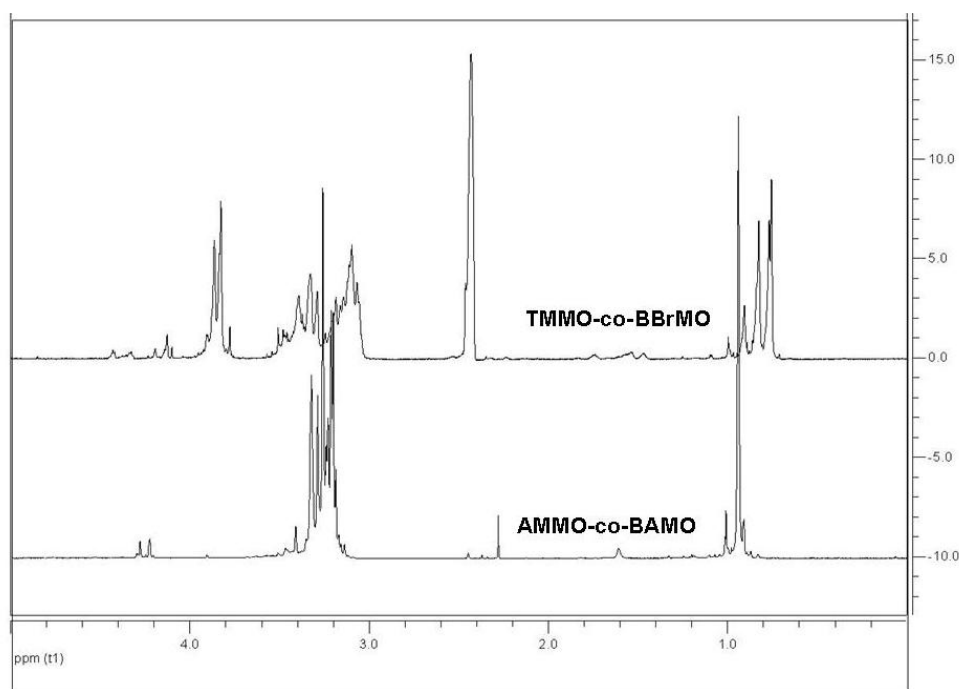
7

Fig. 6. Comparison between ^{1}H-NMR spectra of AMMO-co-BAMO and TMMO-co-BBrMO.

Conclusions

pAMMO and p(AMMO-co-BAMO) 75/25 were successfully prepared by a two-step synthesis; after TMMO homopolymerization (or its copolymerization with BBrMO), the azide groups were introduced on the polyoxetanes by displacement of the tosyloxy (and bromine) groups. This procedure is preferred to that involving the polymerization of the azide monomers, in view of the safety of the process. However, an optimization of the polymerization conditions is needed, since the properties of the final energetic materials depend mostly on this step. For this reason, the present work was mainly focused on the polymerization step.

In presence of a TFB complex and a polyol, cationic homo- and copolymerization of TMMO leads to hydroxyl-terminated polyoxetanes. In particular, a strict control on the OH equivalent was reached using TFBTHF as catalyst. On the contrary, when TFBE was used, termination reactions were found to occur and to lead to non-hydroxyl terminated chains. Actually, the reasons of such different behavior have not been clarified and will be faced in a future work. The role of the initiator has to be carefully examined to explain why none of the catalysts is able to drive the reaction through the desired "living" mechanism. Finally, the azidation was performed with good yield and reasonably short reaction times for both polyoxetane substrates. The molecular weights and OH contents of the products are in the range needed for a good solid fuel binder.

Experimental

Monomers

TMMO was synthesized and purified, as described elsewhere (Rose, [8]), from 3-hydroxymethyl-3-methyl oxetane (Sigma-Aldrich, 98%), tosyl chloride (Sigma-Aldrich,

Unauthenticated
Download Date | 7/30/18 4:39 AM

98%), and pyridine (Carlo Erba, 99%), dried on NaOH and distilled at atmospheric pressure. FT-IR spectrum of TMMO. ν (cm^{-1}): 2,960 (ν_{as} CH$_3$), 2,926(ν_{as} CH$_2$), 2,872 (ν_s CH$_2$), 1,602 (ν C-C aromatic ring), 1,462 (δ CH$_2$), 1,356 (ν_{as} S(=O)$_2$), 1,188 (ν_s S(=O)$_2$), 110(δ_s C-H aromatic ring), 976 (ν_{as} C-O-C, ν_{as} S-O-C), 836 (ν_{as} C-C-O oxetanic ring, , ν_s S-O-C), 668 (ω C-H aromatic ring). ^{1}H-NMR spectra of TMMO (DMSO-d$_6$, 600 MHz): δ (ppm), 7.81-7.48 (4H, dd, aromatic ring), 4.23-4.17 (4H, dd, oxetanic ring), 4.10 (2H, s, CH$_2$OTs), 2.40 (3H, s, CH$_3$ aromatic ring), 1.16 (3H, s, CH$_3$); m.p.=62.4°C.

BBrMO was synthesized, as described elsewhere (Farthing [9]), from 2,2-bisbromomethyl-3-bromo-propan-1-ol (DSBG Israel, 98%), sodium hydroxide (Sigma-Aldrich, >98%) and anhydrous ethanol (Carlo Erba). FT-IR and ^{1}H-NMR analysis confirmed the nature of the product. FT-IR spectrum of BBrMO: ν (cm^{-1}) 2,963 (ν_{as} CH$_2$), 2,877 (ν_s CH$_2$), 1,432 (δ CH$_2$), 1,238 (ω CH$_2$Br), 1,207 (ν_s C-O-C), 981 (ν_{as} C-O-C), 881 (ν_s C-C-O ring), 656 (ν C-Br). ^{1}H NMR spectrum of BBrMO in CDCl$_3$: δ (ppm) 3.93 (s, 4H, CH$_2$Br), 4.34 (s, 4H, CH$_2$O).

Polymerization

Catalyst: boron trifluoride etherate (TFBE) (Sigma-Aldrich) was distilled under vacuum (46 mmHg, 68-70 °C). boron trifluoride tetrahydrofuranate (TFBTHF) (Sigma-Aldrich) was used as received.

Co-Catalyst, polyol: 1,4 butanediol (BDO) (Sigma-Aldrich, 99%) was distilled under vacuum (2 mmHg, 72-73 °C) and stored over silica gel. Glycerol (GLO) (Sigma-Aldrich, 99%) was distilled under vacuum (8 mmHg, 140 °C, respectively) and stored over silica gel. 1,1,1 tris(hydroxymethyl)ethane (Sigma-Aldrich, 99%) was used as received.

Solvent: Dichloromethane (Carlo Erba) was dried on P$_2$O$_5$ and distilled at atmospheric pressure.

pTMMO and TMMO-co-BBrMO: A 100 cc flask, kept under nitrogen atmosphere and at room temperature, was fed with anhydrous and freshly distilled methylene chloride (5 mL), boron trifluoride etherate and 1,4-butanediol (the amounts of the initiating system for each test are listed in (Table 1-2) and stirred for 3 hours. Then a solution of 10 g of purified TMMO in 15 mL of methylene chloride (9.5 g of TMMO and 3 g of BBrMO in 20 mL of DCM, for copolymerizations) was introduced drop by drop in about 3 hours, by keeping the flask at room temperature. All the polymerization reactions were stirred for further 48 hours. Then, the polymer was recovered by solvent evaporation, washed twice with water and twice with a mixture 50/50v water/methanol and finally dried under high vacuum at 100 °C overnight. Hard-glassy materials were recovered with very high yields both for the homo and the copolymers (Table 1-2). FT-IR and ^{1}H-NMR analysis confirmed the nature of the products. FT-IR spectrum of pTMMO. ν (cm^{-1}): 2,881 (ν_s CH$_2$), 1,602 (ν C-C aromatic ring) , 1,462 (δ CH$_2$), 1,356 (ν_{as} S(=O)$_2$), 1,179 (ν_s S(=O)$_2$), 1,100 (δ_s C-H aromatic ring), 968 (ν_{as} C-O-C, ν_{as} S-O-C), 845 (ν_{as} C-C-O oxetanic ring, , ν_s S-O-C), 668 (ω C-H aromatic ring). ^{1}H-NMR spectrum of pTMMO (CDCl$_3$ –d$_3$, 600 MHz): δ (ppm), 7.76-7.35 (4H, dd, aromatic ring), 3.80(2H, s, CH$_2$OTs), 3.08 (2H, s, CH$_2$O main chain), 2.42 (3H, s, CH$_3$ aromatic ring), 0.75 (3H, s, CH$_3$). FT-IR of TMMO-co-BBrMO. ν (cm^{-1}): 2,872 (ν_s CH$_2$), 1,602 (ν C-C aromatic ring) , 1,462 (δ CH$_2$), 1,356 (ν_{as} S(=O)$_2$), 1,100(δ_s C-H aromatic ring), 976 (ν_{as} C-O-C, ν_{as} S-O-C), 836 (ν_{as} C-C-O oxetanic ring, , ν_s S-O-C),

668 (ω C-H aromatic ring), 605 (ν C-Br). ^{1}H-NMR spectra of TMMO-co-BBrMO: δ (ppm) 4.34 (end OH(acetylated)- BBrMO),4.15-4.13 (end OH(acetylated)- TMMO), 3.83 (CH$_2$OTs), 3.33 (CH$_2$-BBrMO), 3.10 (CH$_2$O-TMMO), 2.43 (arylic CH$_3$- TMMO), 1.58 (CH$_2$-THF), 0.76 (CH$_3$-TMMO).

Determination of OH functionalities

Titration: 5 g of the polymer were dried under high vacuum, 75 °C for 3 hours and dissolved in 50 mL of 1,2-dichloroethane. 3 mL of N-methyl imidazole and 10 mL of acetylation reagent (14%vol of acetic anhydride in 1,2-dichloroethane) were added in a flask and heated at 45 °C for 20 minutes. Then 3 mL of water were added in order to hydrolyze the excess of acetic anhydride to acetic acid and the solution was stirred and heated to 45 °C for further 10 minutes. After cooling, 100 mL of a mixture 50/50v methanol/chloroform and some drops of indicator (Thymol Blue) were added to the solution. Finally the mixture was titrated by an alcoholic solution of sodium hydroxide 0.25 N. The equivalent grams of OH were calculated by difference from a blank sample.

^{1}*H-NMR:* 20-25μL of trifluoroacetic anhydride were directly added to the NMR tube-test in order to convert hydroxyl end groups into ester groups. Then protons of an esterified secondary OH group gave the expected peak around 5.3 ppm while protons of an esterified primary OH groups gave a multiplet around 4.5 ppm (Biedron et al. [10]).

Azidation of polymers

The azidation was carried out in 500 cc flask, kept under nitrogen atmosphere and equipped with a magnetic stirrer and a condenser. 25 g of polymer and 200 mL of dimethylsulfoxide were fed in the flask, the temperature increased up to 80 °C, then the required amount of NaN$_3$ (molar excess=1.2) was introduced into the flask and the temperature raised to 95 °C. After 16h, the azide-polymer was precipitated from the solution by water addition, washed and dried under vacuum at 110 °C overnight. FT-IR spectrum of poly-AMMO. ν (cm^{-1}) 3,349 ($\nu_1+\nu_2$ N$_3$) 2,965 (ν_{as} CH$_2$), 2,872 (ν_s CH$_2$), 2,189 (ν C-N), 2,105 (ν_{as} N$_3$), 1,452 (δ CH$_2$), 1,382 (δ_s CH$_3$), 1,350 (ω CH$_2$), 1,294 (ν_s C-O-C), 1,109 (ν_{as} C-O-C), 686 (N$_3$ bend). ^{1}H-NMR spectrum of poly-AMMO (CDCl$_3$, 300 MHz). δ (ppm); 0.94 (3H, s, CH$_3$), 3.21 (4H, m, CH$_2$O), 3.25 (3H, s, CH$_2$N$_3$). FT-IR AMMO-co-BAMO.ν (cm^{-1}) 3,352 ($\nu_1+\nu_2$ N$_3$) 2,965 (ν_{as} CH$_2$), 2,872 (ν_s CH$_2$), 2,189 (ν C-N), 2105 (ν_{as} N$_3$), 1,445 (δ CH$_2$), 1,382 (δ_s CH$_3$), 1,295 (ν_s C-O-C), 1,100 (ν_{as} C-O-C), 686 (N$_3$ bend). ^{1}H-NMR spectrum of AMMO-co-BAMO (CDCl$_3$–d$_3$, 300 MHz). δ (ppm) 4.28 (end OH(acetylated)- BAMO), 4.23 (end OH(acetylated)- AMMO), 3.27 (CH$_2$O-CH$_2$N$_3$ 0.95 (CH$_3$-AMMO).

Instrumentation

The newly synthesized polymers and precursors were characterized by FT-IR spectroscopy (on a Bruker Tensor 27), ^{1}H-NMR (on VXR300 and INOVA600 instruments) and thermogravimetry (on a TA Q500 apparatus) with a scanning rate of 10 °C/min until 400 °C. The molecular weight of the polymers was measured from solutions in CHCl$_3$ (2 mg/mL) by using a GPC apparatus Jasco PU-1580, equipped with PL Mesopore column, and calibrated with low polydispersity polystyrene standards.

References

[1] Gaur, B.; Lochab, B.; Choudary, V.; Varma, I.K. *J. Macromol. Sci.,* **2003**, *43*, 505.

[2] Murali Mohan, Y.; Mani, Y.; Modana Raju, K. *Designed Monomers and Polymers,* **2006***, 9,* 201.

[3] Cheradame,H.; Andreolety,J-P.; Rousset, E. *Makromol.Chem..* **1991**, *192*, 901.

[4] Barbieri, U.; Polacco, G.; Massimi, R. *Macromol. Symp.,* **2006***, 234,* 51.

[5] Barbieri, U.; Polacco, G.; Paesano, E. *Prop., Expl. and Pyrotech.*, **2006,** *31 (5),* 369.

[6] Penczek, S.; Cypryk, M.; Duda A.; Kubisa P.; Slomkowski S. *Prog. Polym. Sci.*, **2007**, *32*, 247.

[7] Kubisa, P.; Bednarek, M.; Biedron T.; Biela T.; Penczek S. *Macromol. Symp.,* **2000***, 153,* 217.

[8] Rose, N.G.W. *Tetrahedron*, **2001**, *57*, 1497.

[9] Farthing, A.C. *J. Chem. Soc.*, **1955**, 3648.

[10] Biedron T.; Kubisa P.; Penczek S. *J. Polym. Sci: Part A: Polym Chem.,* **1991**, *29*, 619.