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Research paper

Synthesis and Characterization of PolyNIMMO-HTPB-polyNIMMO Triblock Copolymer as a Potential Energetic Binder

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Abstract: Triblock copolymer polyNIMMO-HTPB-polyNIMMO was synthesized by cationic ring opening polymerization of NIMMO (3-nitratomethyl-3-methyloxetane) in the presence of hydroxyl-terminated polybutadiene catalyzed by $\text{BF}_3 \cdot \text{OEt}_2$. The polymer was characterized by FT-IR, ^1H NMR, ^{13}C NMR spectroscopy, and GPC. DSC was used to investigate the thermal behaviour of the triblock copolymer and its exothermic decomposition peak was found to be at 215 °C. All of the results indicated that the triblock copolymer polyNIMMO-HTPB-polyNIMMO might serve as a potential energetic propellant binder.

Keywords: triblock copolymer, cationic ring opening polymerization, polymer, DSC

1 Introduction

Hydroxyl-terminated polybutadiene (HTPB) is an oligomer of butadiene terminated at each end with a hydroxyl functional group [1]. As a telechelic polymer, HTPB is a binder with a low T_g (−75 °C), good transparency, low viscosity, ageing resistance, and wonderful mechanical properties [2]. HTPB has a variety of applications, one of the typical examples being the production of casting elastomer, which is the raw material of tyres. It can also be used in construction, shoe-making, rubbery products, adhesive, casting, waterproofing, racetracks, as well as a modified solvent for rubber and epoxy resin [3-6].

An important application of HTPB is in solid rocket propellants and polymer-bonded explosives (PBX). In an HTPB-based plastic-bonded explosive, the

HTPB binds the explosive powder into a solid but elastic mass. The elastic mass tends to absorb shock, making the PBX very insensitive to accidental detonation [7, 8]. In solid rocket propellants, the HTPB binds the oxidizing agent and other ingredients together. Cured polyurethane acts as a fuel in such mixtures. HTPB reacts with isocyanates to form three-dimensional network structures [9-11]. The polyurethane network system shows excellent mechanical properties. However, HTPB is inert, reducing the overall energy output.

In recent years, the replacement of HTPB by energetic polymeric binders such as glycidyl azide polymer (GAP) [12], poly[(3-azidomethyl)-3-methyloxetane] (polyAMMO) [13], poly[3,3-bis(azidomethyl)oxetane] (polyBAMO) [14], polyglycidyl nitrate (PGN) [15] and poly[(3-nitratomethyl)-3-methyloxetane] (polyNIMMO) [16] to develop advanced rocket propellants is a new trend. PolyNIMMO is an energetic polymer with high energy output and good compatibility with highly energetic oxidizers.

Although polyNIMMO has a higher T_g (-30 °C) and it is no better for use as a propellant binder, it improves the burning rate of propellants. Therefore, preparation of a block copolymer of HTPB and polyNIMMO may provide a more suitable energetic propellant binder. Recently, some efforts have been made to balance the energy and mechanical properties of energetic binders. For example, the triblock copolymers GAP-HTPB-GAP, GAP-PEG-GAP, PGN-PCL (polycaprolactone)-PGN and PGN-HTPB-PGN were prepared to improve the mechanical and thermal properties of GAP or PGN [2, 17-20].

Herein we describe an attempt to synthesize a novel energetic propellant binder, polyNIMMO-HTPB-polyNIMMO, based on HTPB and polyNIMMO.

2 Experimental

2.1 Materials

Hydroxyl-terminated polybutadiene (average $M_n \sim 5900$ by GPC) was obtained from the Liming Research Institute of Chemical Industry (Luoyang, Henan Province, China). NIMMO was prepared based on a reported method [21]. Borontrifluoride etherate ($\text{BF}_3 \cdot \text{OEt}_2$) and dichloromethane were obtained from the Xi'an Chemical Reagents Factory (Xi'an, Shaanxi Province, China).

2.2 Characterization methods

FT-IR spectra were measured with a Bruker Tensor 27 instrument (KBr pellets) with a resolution of 4 cm^{-1} in the range $400\text{--}4000 \text{ cm}^{-1}$. ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker 500 MHz instrument using CDCl_3 as

a solvent. GPC was conducted using a Waters GPC instrument equipped with four Ultrastaygel columns (10 nm, 50 nm, 100 nm and 1000 nm), a refractive index detector and a Datamodule 730. Tetrahydrofuran was used as the mobile phase at a flow rate of $0.8 \text{ mL} \cdot \text{min}^{-1}$ through the columns at $30 \text{ }^\circ\text{C}$. A series of PS standards were used to generate a GPC calibration curve. DSC analyses were conducted with a TA Instruments DSC Q1000 to thermally characterize the samples using a heating/cooling rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$.

2.3 Synthesis of polyNIMMO-HTPB-polyNIMMO

Moisture-free HTPB (10 g) in CH_2Cl_2 (20 mL) was placed at $25 \text{ }^\circ\text{C}$ in a 100 mL three-necked round-bottomed flask fitted with a CaCl_2 guard-tube and nitrogen inlet. $\text{BF}_3 \cdot \text{OEt}_2$ (0.5 mL) was then added to the flask and stirred for 30 min. NIMMO (5.72 g) in CH_2Cl_2 (20 mL) was added dropwise to the stirred solution over a period of 2 h and the reaction was continued at $25 \text{ }^\circ\text{C}$ for 48 h. The solvent and unreacted monomers were removed by vacuum distillation. The molecular weight distribution and the composition of the synthesized copolymer were determined using GPC and NMR. Optimization of the parameters which affect the synthesis of the tri-block copolymer is summarized in Table 1. To investigate the effect of the monomer concentration on the tri-block copolymer length the feed ratio of NIMMO to HTPB was increased.

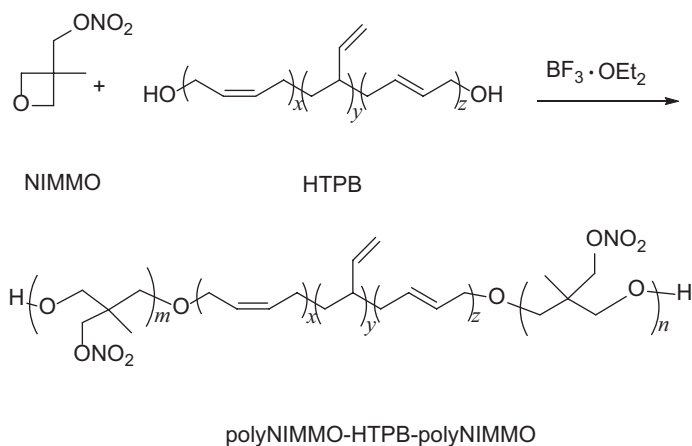
Table 1. Optimization of the synthesis of polyNIMMO-HTPB-polyNIMMO

Entry	HTPB [g]	$\text{BF}_3 \cdot \text{OEt}_2$ [mL]	NIMMO [g]	Solvent	M_n [g/mol]
1	10	0.5	5.72	CH_2Cl_2	9100
2	10	0.5	11.44	CH_2Cl_2	12500
3	10	1.0	5.72	CH_2Cl_2	8900
4	10	0.5	5.72	CHCl_3	9000
5	10	0.5	5.72	$\text{C}_6\text{H}_5\text{CH}_3$	6700

3 Results and Discussion

3.1 Characterization of polyNIMMO-HTPB-polyNIMMO

The polyNIMMO-HTPB-polyNIMMO was synthesized by cationic ring opening polymerization of NIMMO with HTPB as initiator and $\text{BF}_3 \cdot \text{OEt}_2$ as catalyst.

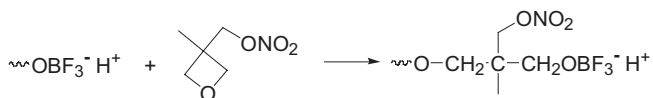
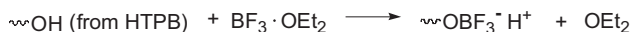


Like ethylene glycol, 1,4-butanediol, and other low molecular weight diols, HTPB and poly(ethylene glycol)s also effectively serve as co-initiators in the ring-opening polymerization of NIMMO in the presence of $\text{BF}_3 \cdot \text{OEt}_2$, to form triblock copolymers of HTPB and polyNIMMO following the activated monomer mechanism [22].

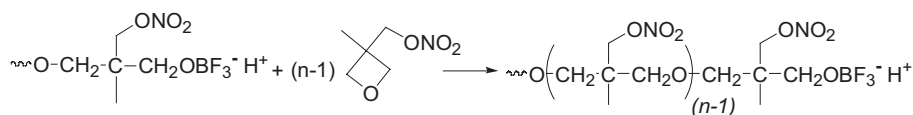
The reaction is sensitive to moisture, so the material should be completely dried. HTPB acts as initiator and attacks the NIMMO epoxy ring while $\text{BF}_3 \cdot \text{OEt}_2$ activates the ring. After opening the epoxy ring, another NIMMO monomer is involved in the copolymerization reaction and becomes attached to the polymer chain. The reaction is continued until all NIMMO monomers have been consumed. The polymers obtained in this process have HTPB blocks in the center of the chain and polyNIMMO blocks on both ends.

NIMMO Polymerization:

Activated monomer Initiation:



Propagation:



Termination:

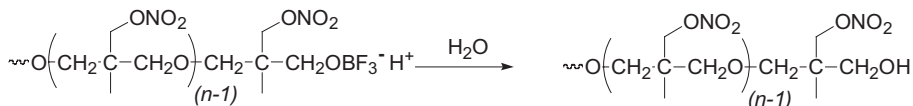


Figure 1. FT-IR spectra of pure HTPB, NIMMO, and polyNIMMO-HTPB-polyNIMMO

Figure 1 shows the FT-IR spectra of pure HTPB, NIMMO, and polyNIMMO-HTPB-polyNIMMO. In the FT-IR spectrum of NIMMO, the symmetric and unsymmetric stretching vibrations of NO_2 were observed at 1633 cm^{-1} and 1286 cm^{-1} . The peaks observed at 2878 cm^{-1} and 983 cm^{-1} were attributed to the stretching vibrations of C–H and C–O. The FT-IR spectrum of the triblock copolymer polyNIMMO-HTPB-polyNIMMO exhibited the same characteristic peaks as NIMMO at 2846 cm^{-1} , 1634 cm^{-1} , and 1281 cm^{-1} ; the peak at 1103 cm^{-1} was attributed to the stretching vibration of C–O in the chain. Moreover, the strong absorbance band at 2916 cm^{-1} was attributed to C–H in HTPB. All of these peaks confirm that the tri-block copolymer polyNIMMO-HTPB-polyNIMMO was successfully synthesized.

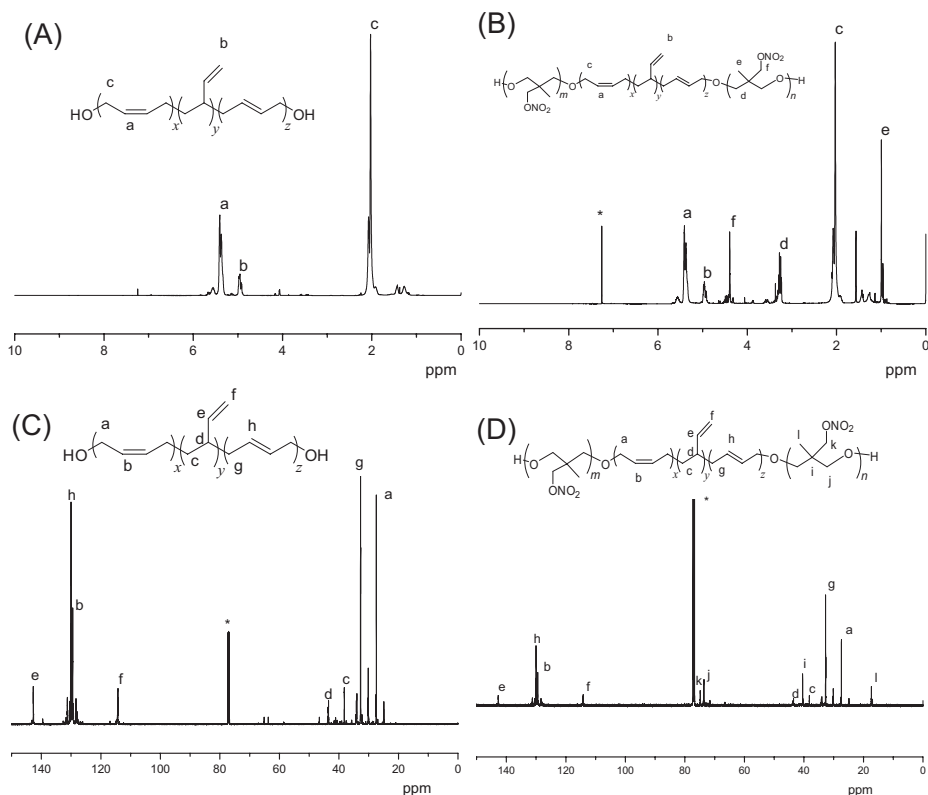


Figure 2. ¹H NMR spectra of (A) HTPB, (B) polyNIMMO-HTPB-polyNIMMO; ¹³C NMR spectra of (C) HTPB, (D) polyNIMMO-HTPB-polyNIMMO

The structures of HTPB and polyNIMMO-HTPB-polyNIMMO were also characterized by ¹H NMR and ¹³C NMR spectroscopy, as presented in Figure 2. As shown in Figure 2A, the signals observed at 2.02-2.07 ppm were attributed to the methylene protons (denoted c) of the main chain. The signals at 4.93-4.97 ppm were due to the terminal ethylene protons (denoted b) of the side chain. The signals at 5.36-5.40 ppm were attributed to the ethene protons (denoted a) of the main chain [23]. On the other hand, the ¹H NMR spectrum of polyNIMMO-HTPB-polyNIMMO exhibited the same characteristic signals as HTPB and polyNIMMO at 0.98 ppm (denoted e), 3.20-3.30 ppm (denoted d) and 4.39 ppm (denoted f), as shown in Figure 2B. The copolymerization reaction was also confirmed by the ¹³C NMR spectra. As shown in Figure 2C, the resonances of the methylene carbons (denoted a, g, c) in the main chain were observed at

27.2 ppm, 32.4 ppm and 37.9 ppm, respectively. The resonances of the methine carbons (denoted d) in main chain, were observed at 43.2 ppm. Meanwhile, the resonances of the ethylene carbons in the main chain were observed at 129.1 ppm (denoted b) and 129.6 ppm (denoted h). The resonances of the carbons in the side chain were observed at 114.1 ppm (denoted f) and 142.2 ppm (denoted e). Moreover, the ^{13}C NMR spectrum of polyNIMMO-HTPB-polyNIMMO exhibited the same characteristic signals as HTPB and polyNIMMO, at 17.5 ppm (denoted l), 40.5 ppm (denoted i), 73.7 ppm (denoted j) and 74.9 ppm (denoted k), as shown in Figure 2D.

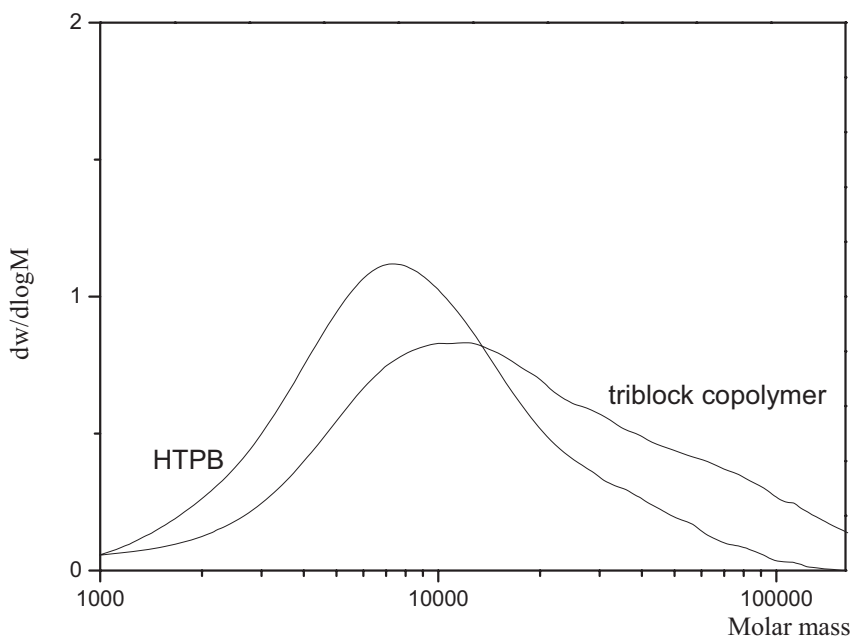


Figure 3. GPC curves of pure HTPB and polyNIMMO-HTPB-polyNIMMO

Figure 3 shows the GPC curves of pure HTPB and polyNIMMO-HTPB-polyNIMMO. It was observed that the synthesized copolymer had a relatively wide molecular weight distribution ($M_w/M_n = 3.50$) and $M_n = 9100$ g/mol. The average molecular weight of the triblock copolymer polyNIMMO-HTPB-polyNIMMO increased from 5900 g/mol ($M_w/M_n = 2.25$) for HTPB to 9100 g/mol ($M_w/M_n = 3.50$) after copolymerization. The GPC result was close to the theoretical molecular weight of polyNIMMO-HTPB-polyNIMMO (around 8832 g/mol). These results confirmed the successful synthesis of the triblock copolymer polyNIMMO-HTPB-polyNIMMO.

3.2 Properties of polyNIMMO-HTPB-polyNIMMO

Figure 4 shows the DSC glass transition temperature (T_g) curve of polyNIMMO-HTPB-polyNIMMO. The polyNIMMO-HTPB-polyNIMMO triblock copolymer exhibited a very low glass transition temperature ($-76\text{ }^\circ\text{C}$). The T_g value is much lower than that of polyNIMMO itself ($-30\text{ }^\circ\text{C}$). The flexible groups of the HTPB block in the copolymer have reduced the T_g of polyNIMMO-HTPB-polyNIMMO to below that of polyNIMMO. Furthermore, the triblock copolymer has a single glass transition temperature. The single T_g of polyNIMMO-HTPB-polyNIMMO triblock copolymer indicates that there is compatibility between the polyNIMMO and HTPB blocks in the triblock copolymer.

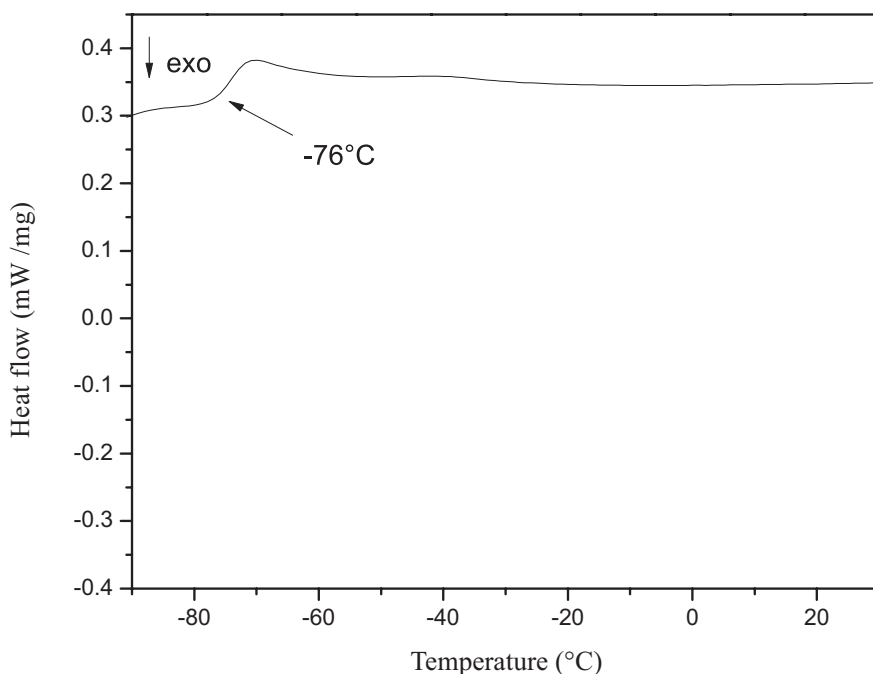


Figure 4. DSC T_g curve of polyNIMMO-HTPB-polyNIMMO

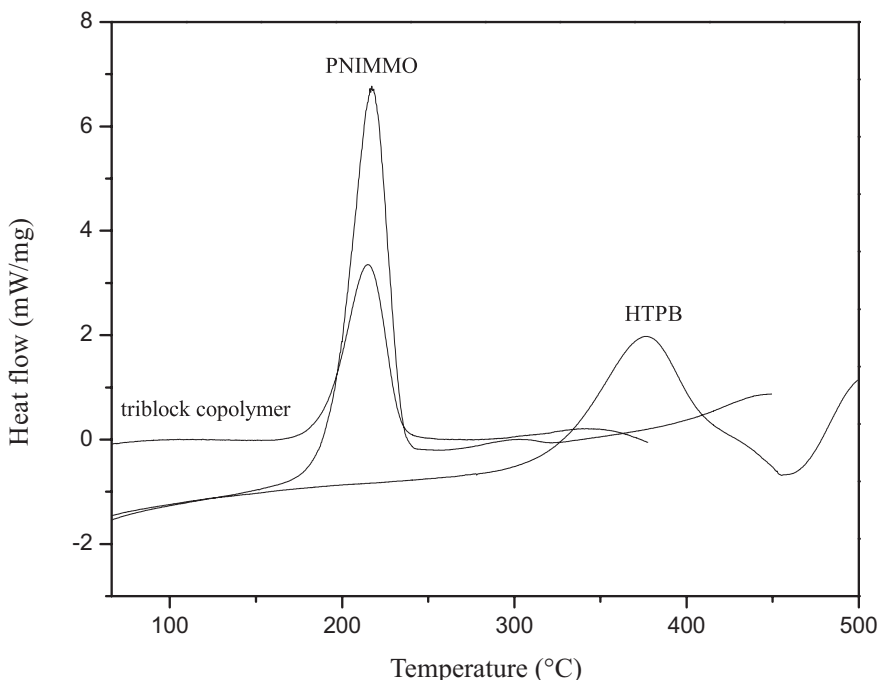


Figure 5. DSC curves of polyNIMMO, HTPB and the triblock copolymer

The thermal stability of energetic materials plays an important role in their preparation, processing, storage, and application. Hence, it is important to investigate the thermal decomposition behaviour for a potential energetic binder. In order to investigate the dependence of the copolymer structure on its thermal behaviour, DSC measurements were performed. Figure 5 shows the DSC curves of polyNIMMO, HTPB and the triblock copolymer. As may be seen, HTPB has certain advantage in terms of thermostability over the energetic polymers. The DSC curve of polyNIMMO-HTPB-polyNIMMO triblock copolymer is similar to the DSC curve of polyNIMMO. The degradation of polyNIMMO is initiated *via* the cleavage of the nitrate ester groups [24]. In polyNIMMO-HTPB-polyNIMMO triblock copolymer, an exothermic decomposition peak is observed around 215 °C, corresponding to the degradation of the polyNIMMO energetic segment.

4 Conclusions

Triblock copolymer polyNIMMO-HTPB-polyNIMMO was synthesized by cationic ring opening polymerization of NIMMO (3-nitratomethyl-3-methyloxetane) in the presence of hydroxyl-terminated polybutadiene catalyzed by $\text{BF}_3 \cdot \text{OEt}_2$. The polymer was characterized by FT-IR, ^1H NMR, ^{13}C NMR spectroscopy, and GPC. The T_g value of polyNIMMO-HTPB-polyNIMMO triblock copolymer is much lower than that of polyNIMMO itself. DSC was used to investigate the thermal behaviour of the triblock copolymer and its exothermic decomposition peak was found to be at 215 °C. This energetic binder, based on HTPB and NIMMO, can be cured by curing agent N-100 and its mechanical properties can be better than polyNIMMO. All of these results indicated that the triblock copolymer polyNIMMO-HTPB-polyNIMMO might serve as a potential energetic propellant binder.

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