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Synthesis and characterization of hydroxyl terminated poly(butadiene)-*g*-poly(glycidyl azide) copolymer as a new energetic propellant binder

Mehmet S. Eroğlu [1], Baki Hazer [1,2], Olgun Güven [3]

[1] TÜBİTAK-Marmara Research Center, Research Institute for Basic Sciences, Department of Chemistry, P.O. Box 21, 41470 Gebze, Turkey
[2] Karadeniz Technical University, Department of Chemistry, 61080 Trabzon, Turkey
[3] Hacettepe University, Department of Chemistry, 06532 Beytepe, Ankara, Turkey

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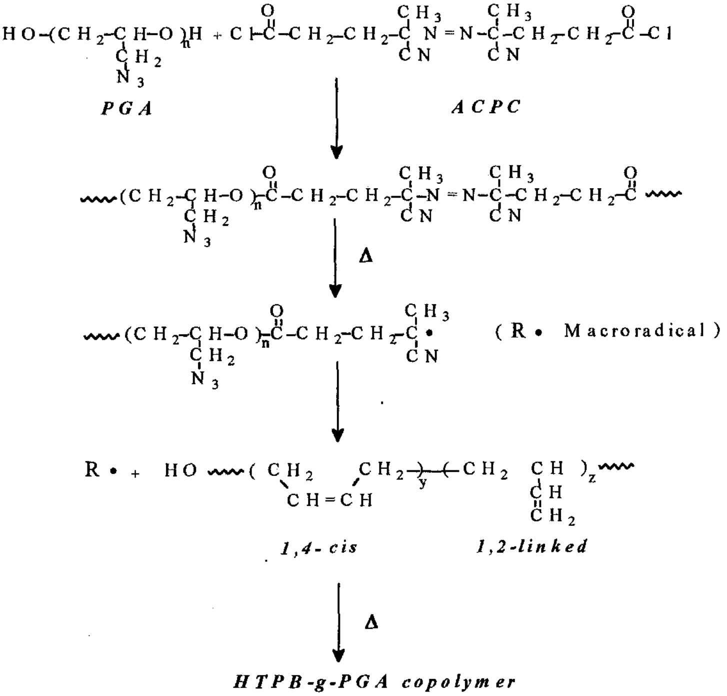
Summary

Poly(glycidyl azide), PGA,was grafted onto Hydroxyl Terminated Poly(butadiene), HTPB, via free radical mechanism. PGA-macro azoinitator and HTPB polymer mixture was casted from solution and the polymer film was kept at 90 ^{o}C for 4 hours. The grafted polymer was isolated from the product by fractional precipitation and characterized by NMR and FT-IR spectroscopy. Graft copolymer structure was also confirmed that volume ratio of nonsolvent to the solution of the graft copolymer was between those of corresponding homopolymers. TGA traces of the block polymers were containing two different maxima at 253 ^{o}C (for PGA units) and 469 ^{o}C (for HTPB units). Because of the incompatibility of the blocks, DSC curve showed two T_g's which belong to the related segments.

Introduction

The typical composite solid propellants may be prepared by crosslinking of a polymeric binder with conventional isocyanates in the presence of solid particulate oxidizer material, burning rate catalyst, solid fuel plasticizer and other minor ingredients. The resultant elastomeric network has the polyurethane structure. The prepolymers used for binding materials and fuel should have a suitable fludity at an ambient temperature in order to secure a high castability and high holding capacity of solid ingredients within a three dimensional network [1-4]. On the other hand, a propellant grain should have good mechanical and combustion properties. The widely used polymeric binder in composite propellant technology is Hydroxyl Terminated Poly(butadiene), HTPB which has unique physico-chemical properties.
Recently, aside from providing favorable mechanical properties of HTPB, a lot of work has been done for the sysnthesis of new energetic materials. Poly(glycidyl azide), PGA is a high energetic polymer synthesized during the last decade [5-9]. This polymer contains energetic pendant azide ($-N_3$) groups on the polyether main chain. It is in fact a unique energetic material with positive heat of formation (+975 kJ/kg) capable of self burning at elevated pressures [10]. Because of the superior thermal properties, PGA is potential candidates to prepare high burning rate, high spscific impuls and smokeless propellants. Although it has relatively higher glass transition temperature (T_g= -48 ^{o}C) compared to HTPB (T_g= -78 ^{o}C). In our previous work, styrene and vinyl acetate copolymerization with macroinitiators containing PGA units was studied [11].

In the present study, regarding the unique thermal properties of PGA and physico-chemical properties of HTPB at relatively low temperatures attempts were made to synthesis and characterization of HTPB-g-PGA copolymer in order to use in the preparing of rocket propellants. Taking into account of the advantages of individual homopolymer segments, HTPB-g-PGA copolymer is expected to have promising application as a new energetic binder in the rocket fuel technology. This copolymerization is based on the principles that the macroradicals formed by thermal decomposition of these PGA macroinitiators may attack to double bonds on the main chain or pendant vinyl groups or they may abstract allylic hydrogen forming an allylic radical. A lot of work have been done to undertake the grafting of the polymers having double bonds on the main chain or pendant vinyl groups via the macroradicals [12-14]. This phenomenon can be proposed as follows,



Experimental

Materials

PGA was synthesized by the reaction of PECH with NaN_3 following the procedure described in reference [6-9]. It has a number average molecular weight of 2200 g/mol as determined by Vapour Phase Osmometer (VPO). Hydroxyl value of PGA was determined as 0.94 meq/g according to the method cited in reference [15]. The elemental analysis results of PGA is as follows,

	C (%)	N(%)	H(%)
Calculated	36.36	42.42	5.05
Found	35.95	42.23	5.11

PECH was supplied from 3M (USA) under the trade name of HX-102 and used without further purification. Its molecular weight was 1810 g/mol and hydroxyl value was 1.14 meq/g.Sodium azide was supplied from Merck and used as received. 4,4' azobis(4-cyanopentanoic acide), ACPA was purchased from Fluka as better than 98% purity. ACPA was converted to the acid chloride derivative , 4,4' azobis(4-cyanopentanoyl chloride), ACPC with m.p = 92 ^{o}C.

HTPB was supplied from ARCO (USA) under the trade name of R 45-HT. Number average molecular weight and OH equivalent weight of HTPB were determined as 2710 g/mol (VPO) and 0.7 meq/g respectively.

Synthesis of Poly(glycidyl azide) Macroinitiator(MI-PGA)

A solution of 10 mmol ACPC in 50 ml of benzene was gradually added to the mixture of 10 mmol of PGA, 10 mmol triethyl amine and 200 ml benzene by stirring at 0 ^{o}C for 30 min in dark. The reaction mixture was stirred 3 hours at 0 ^{o}C and allowed to warm up to room temperature by stirring overnight in dark. Then the mixture was filtered, washed with 15 wt-% of HCl aqueous solution and dried over Na_2SO_4. Solvent was evaporated. The liquid was dissolved in 20 ml acetone and poured into 500 ml petroleum ether. The yellowish viscouse liquid was obtained and dried under vacuum at room temperature. NMR,δ(ppm)=1.7 and 2.3-2.7 (d,CH_3- and m,CH_2- groups of azobis cyanopentanoyl, respectively), 3.4-3.8(d,CH_2- groups in polyether). IR (cm^{-1}), 1120 and 2100 (C-O-C and C-N_3 bonds of polyether, respectively).

Synthesis of HTPB-g-PGA Copolymer

A solution was prepared from a mixture of 0.5 g MI-PGA and 0.5 gr of HTPB in 30 ml $CHCl_3$ (as solvent) according to the cited literatures [14,16]. The solution was stirred for 24 hour and spread onto a glass plate and air-dried. This sample was heated for 4 hours at 90 ^{o}C under nitrogen atmosphere. Unreacted HTPB and PGA were separeted by using the solvent ($CHCl_3$) and nonsolvent (CH_3OH) precipitation technique [17]. The results of grafting procedure are listed in Table 1.

Table 1. Analysis of graft copolymerization

Run No	Code	MI-PGA (g)	HTPB (g)	The ratio of MI-PGA to HTPB	γ[a]	Amount of the fraction in mixture wt-%
1	1/1	0.2503	0.5043	0.4963	0.9	26.97 homo-HTPB
	1/2				2.1	31.89 HTPB-g-PGA
	1/3				>2.3	41.14 homo-PGA
2	2/1	0.5048	0.5073	0.9951	0.9	27.46 homo-HTPB
	2/2				2.1	26.49 HTPB-g-PGA
	2/3				>2.3	46.05 homo-PGA
3	3/1	0.7536	0.5	1.5072	0.9	34.59 homo-HTPB
	3/2				2.5	32.81 HTPB-g-PGA
	3/3				>2.8	32.60 homo-PGA
4	4/1	1.0276	0.5052	2.0341	0.9	29.52 homo-HTPB
	4/2				2.2	22.61 HTPB-g-PGA
	4/3				>2.4	47.87 homo-PGA

[a] By fractional precipitation. Solvent:$CHCl_3$, nonsolvent:Methanol. γ, volume ratio of nonsolvent to solvent 0.9-1.0 for homo HTPB, 3.3 for homo PGA.

Instrumentation

Thermal analysis of samples was carried out by using DuPont 9900 thermal analyser under nitrogen atmosphere and at heating rate of 10 ^{o}C/min. TGA trace and DSC curve of HTPB-g-PGA (run no:4 code:4/2 in Table 1) can be seen in Figure 3 and 4 respectively. IR and NMR spectra of the polymer samples were taken on a Perkin Elmer 177 IR spectrometer and a 200 MHz Bruker-AC 200L NMR spectrometer in $CDCl_3$ respectively. GPC chromatograms were taken by using Waters 510 HPLC Pump with Waters 410 differential refractometer and Waters Styragel HR1 Columns, THF being eluting solvent at 40 °C. Figure 5-a,b,c shows chromatograms of homo HTPB, Homo PGA and HTPB-g-PGA respectively.

Results and Discussion

HTPB-g-PGA copolymers were obtained in moderate yields (Table 1). Fractional precipitation of product confirmed the graft copolymer structure. γ for pure graft copolymers was 2.1-2.5 while 0.9 for HTPB and > 2.4 for PGA. Spectroscopic characterization of block copolymers isolated was also confirmed by the presence of characteristic bands of related block segments. Characteristic bands of the these segments were observed in NMR and IR spectra of copolymer (run no:4 in Table 1) as shown in Figure 1 and 2 .

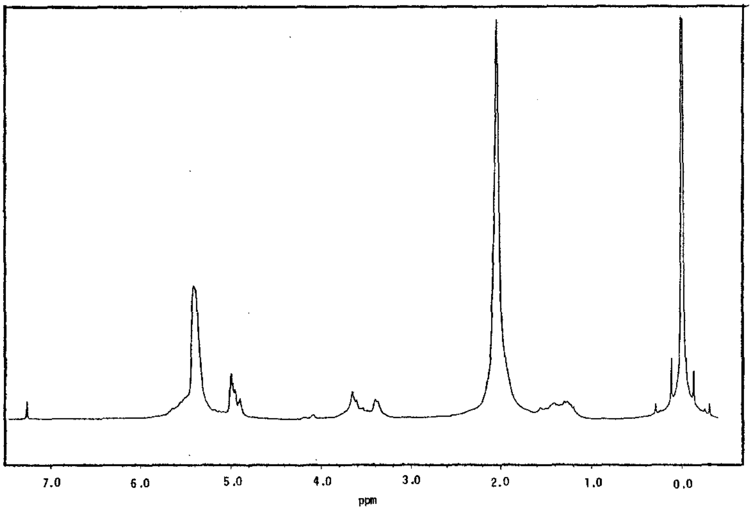


Figure 1. NMR spectrum of HTPB-g-PGA (Run no:4)

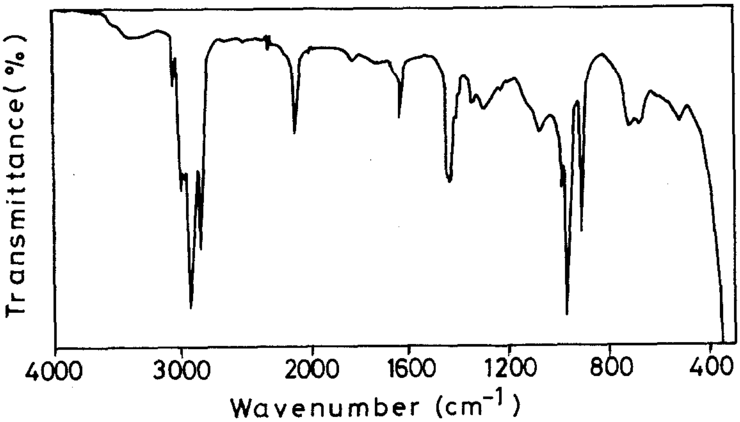


Figure 2. IR spectrum of HTPB-g-PGA (Run no:4)

Figure 1 shows the NMR spectrum of graft copolymer. CH_2- peaks of PGA segment at δ=3.4-3.8 ppm are clearly seen [9]. The -CH= (δ=5.4 ppm), =CH_2 (δ=5.0 ppm) and -CH_2C= (δ=2.0 ppm) signals shown in NMR spectrum of graft copolymer are due to HTPB block.
From the IR spectrum of block copolymer (run no:4 in Table 1), in Figure 2, the sharp peak giving absorbance at 2100 cm^{-1} and the other small peak at 1281 cm^{-1} belong to CH_3-N_3 bonds of PGA segments are observed. Moreover the other absorbance peak of C-O-C ether bridge of PGA block can be seen at 1125 cm^{-1} [18]. The sharp peaks at 910 cm^{-1} and 970 cm^{-1} are du to =$CH_{2\ vinyl}$ and CH=CH_{trans} groups of HTPB respectively. From this spectrum the characteristic peaks giving absorbance at 1640 cm-1 and 720 cm-1 belong to C=C and CH=CH_{cis} bonds of HTPB can be clearly seen [20]. Finally the broad absorbance peak at 3400 cm-1 is due to terminal -OH groups of HTPB.
Thermal characterization of HTPB-g-PGA block copolymers was further achieved by recording their TGA and DSC curves. Figure 3 shows the TGA trace of HTPB-g-PGA copolymer (run no:4 in Table 1) together with the derivative thermogram. Characteristic first step weight loss temperature, 253 ^{o}C corresponding to the stripping of pendant -N_3 groups from the polyether main chain of PGA [10,18,19], is clearly seen in Figure 3. The second main weight loss at 468 ^{o}C observed in Figure 3 is due to the thermal decomposition of HTPB [20]. The small shoulder between two main weight loss observed in derivative thermograms of copolymer is arised from the slightly overlapping of the second stage weight loss peak of PGA and thermal crosslinking peak of HTPB [18-20]. Here distinct peaks representative of thermal degradation of individual homopolymers are observed to be retained during the thermal degradation of corresponding block copolymer.

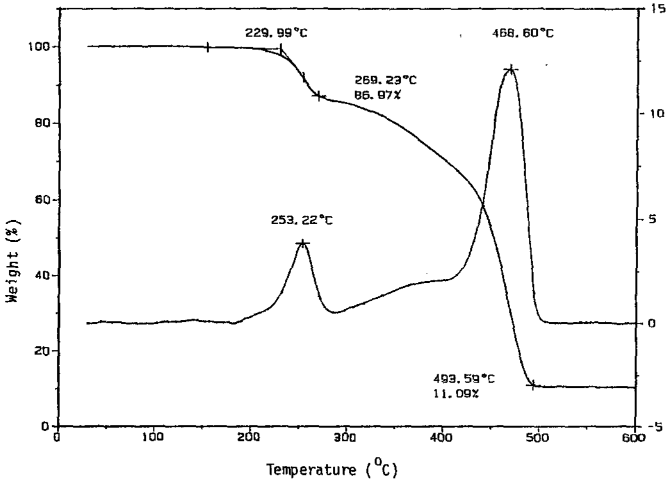


Figure 3. TGA thermogram of HTPB-g-PGA (Run no: 4)

In order to well understand the thermal behaviour of copolymers, T_g traces of copolymers were recorded (Figure 4). As it was expected previously, because of the incompatibility of the blocks, two distict glass transition temperatures representing those of homopolymer segments are observed (run no:4 in Table 1). The slight shifting in T_g value of PGA segment to high temperature side of the thermogram was probably due to the interaction of incompatible segments of the blocks.

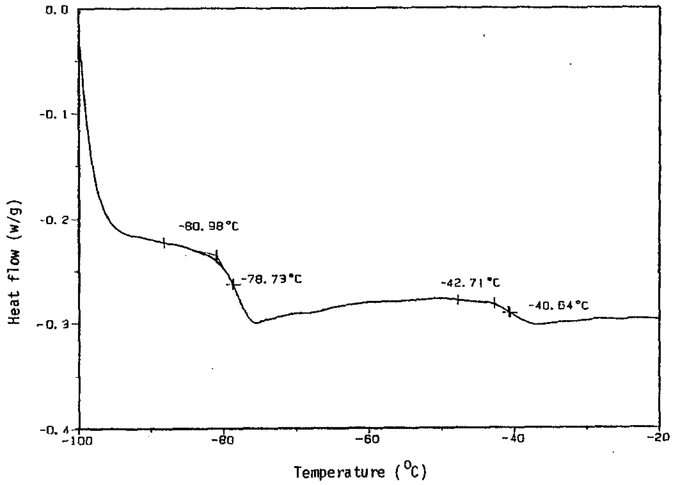


Figure 4. DSC thermogram of HTPB-g-PGA (Run no: 4)

The results of both TGA and DSC studies can be taken as a proof of the presence of blocks of corresponding homopolymers in the backbone.

When we compare GPC chromatograms of HTPB, PGA and HTPB-g-PGA in Figure 5, we observe that there is a slightly difference between elution times of HTPB and graft copolymer chromatograms. This small difference in elution times is characteristic for graft copolymers because grafting segments can not influence in M_n value of main chain in GPC technique.

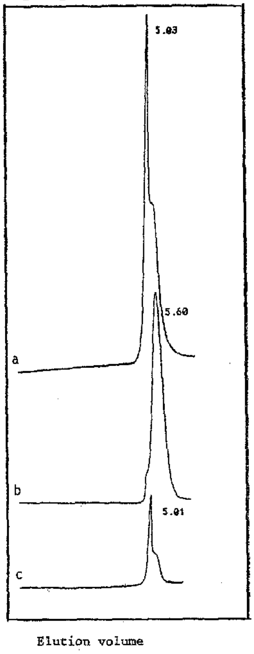


Figure 5. GPC chromatograms of a) Homo-HTPB b) Homo-PGA
c) HTPB-g-PGA (Run no:4)

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