

Preparation and Thermal Characterization of Block Copolymers By Macroazobitriles Having Glycidyl Azide and Epichlorohydrin Moieties

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SYNOPSIS

Poly(glycidyl azide) (PGA) an energetic polymer and polyepichlorohydrin (PECH) were condensed with 4,4' azobis(4-cyanopentanoyl chloride) (ACPC) to prepare macro-azo-initiators. Block copolymers containing each of these polyethers as a block segment combined with polystyrene (PS) or poly(vinyl acetate) (PVAc) have been driven by the polymerization of monomers initiated with this macro-azo-initiators. Thermal properties of block copolymers were investigated with differential scanning calorimetry (DSC) and thermogravimetry. DSC traces showed single glass transition temperatures in between the related segments of copolymers. Dynamic thermogravimetric analysis revealed the individual degradation behaviors of block segments © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Macro-azo-initiators provide a useful means of preparing block copolymers via radical process. Macro-azo-initiators can be prepared by the condensation reactions of a prepolymer with azobis-isobutyronitrile,¹ 4,4' azobis(4-cyanopentanoyl chloride),^{2,3} 4,4' azobiscyanopentanol.^{4,5} For the starting prepolymers of macroazoinitiators, poly(ethylene glycol),^{1,3,6} poly(propylene glycol),^{1,4,5} polybutadiene,⁷ polydimethylsiloxane,⁸ polytetrahydrofuran,^{5,9} polyarylate,¹⁰ and very recently² poly(ethylene adipate), poly(tetramethylene adipate) were reported in terms of copolymerization.

Solid propellant compositions have employed nitroglycerin as an explosive plasticizer, which is a highly energetic plasticizer. Although much success has been achieved with the use of nitroglycerin or its related derivatives in solid propellant compositions, a greater degree of safety in handling and a reduced sensitivity to detonation have been de-

sired.¹¹ Poly(glycidyl azide) (PGA) synthesized by the reaction of polyepichlorohydrin (PECH) and sodium azide (NaN₃), according to the cited references^{12,13} is a new energetic material used in preparing the rocket propellants. The block copolymers carrying PGA and various vinyl polymer segments are expected to have promising applications as a binder in rocket fuel technology. This paper refers to the synthesis of macroinitiators from PGA and its precursor PECH to obtain vinyl block copolymers having PGA and PECH segments.

EXPERIMENTAL

Materials

Styrene and vinyl acetate (VAc) were purified by vacuum distillation. PECH was supplied from 3M (USA) under the trade name of HX-102 and was used without purification. Its molecular weight was 1810 g/mol, and its hydroxyl value was 1.14 meq/g. PGA was synthesized by the reaction of PECH with NaN₃ following the procedure described previously.^{12,13} Its molecular weight was found to be

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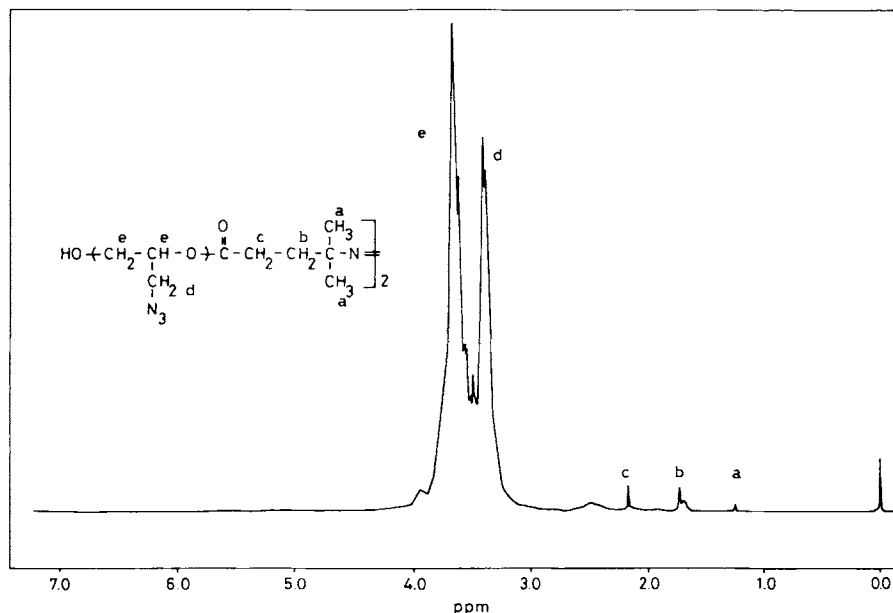


Figure 1 NMR spectrum of MI-PGA.

2200 g/mol by vapor phase osmometer (VPO). 4,4'-azobis(4-cyanopentanoic acid) (ACPA) was purchased from Fluka AG with better than 98% purity. ACPA was converted to the acid chloride derivative, 4,4'-azobis(4-cyanopentanoyl chloride) (ACPC) with m.p. = 97°C.

Instrumentation

Thermal analysis of polymer samples was carried out by using a Du Pont 990 Thermal Analyzer. IR, NMR, and UV spectra of the polymer samples were taken on a Nicolet 210 P FTIR, a 200 MHz Bruker-AC 200L NMR, and a Varian DMS 90 UV-VIS spectrometer. Molecular weight of PGA and PECH were determined by using a Knauer Vapor Phase Osmometer.

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

To the mixture of 20 mmol of PGA having —OH terminals, 20 mmol of triethyl amine and 200 mL of benzene, 10 mmol of ACPC in 50 mL of benzene was gradually added by stirring at 0°C for 30 min, in the dark. After 3 h stirring at 0°C the reaction mixture was allowed to warm up to room temperature and was stirred overnight, in the dark. Then the mixture was filtered, washed with 15 wt % of HCl aqueous solution and was dried over Na₂SO₄. Solvent was evaporated. The liquid was dissolved in 20 mL of acetone and was poured into 500 mL of

methanol. Pale yellowish viscous liquid was obtained and was dried under vacuum at room temperature. NMR; δ (ppm) = 1.7 and 2.3–2.7 (*c*, CH₃⁻ and *m*, CH₂⁻ groups of azobis cyanopentanoyl, respectively); 3.4–3.8 (*d*, CH₂⁻ groups in polyether); IR (cm⁻¹); 1120 and 2100 (C—O—C and C—N₃ bonds of polyether, respectively). Figure 1 shows an NMR spectrum of PGA macroinitiator (MI-PGA).

Synthesis of PECH Macroinitiator (MI-PECH)

MI-PECH was prepared by the procedure described above by using 20 mmol of PECH, 10 mmol of ACPC, and 20 mmol of triethyl amine. The viscous liquid obtained was dried under vacuum at room temperature. NMR, δ (ppm) = 1.7 and 2.3–2.7 (*d*, CH₃⁻ and *m*, CH₂⁻ groups of azobis cyanopentanoyl, respectively); 3.4–3.8 (*s*CH₂⁻ groups of polyether); IR (cm⁻¹), 1120 (C—O—C bonds of polyether). Figure 2 shows a Fourier transform (FTIR) spectrum of MI-PECH.

Polymerization of Vinyl Monomers with MI-PGA and MI-PECH

In a typical example 4.98 g of styrene was polymerized by using 1.0 g of MI-PGA as initiator in a pyrex tube under N₂ at 70°C. After a fixed time of reaction, the content of the pyrex tube was poured into a large amount of methanol. The polymer precipitated was dried under vacuum at room temperature for 2 d. PGA-*b*-PS block copolymer (*-b-*) was separated from related homopolymers by fractional precipitation,

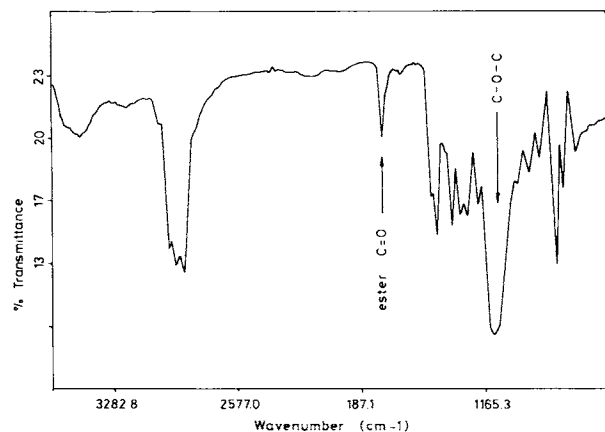


Figure 2 FT-IR spectrum of MI-PECH.

which used CHCl_3 as a solvent and methanol as a nonsolvent. Volume ratio of the nonsolvent to solvent γ of the block copolymer was also determined. Table I indicates the polymerization results and conditions. Whole reactions including synthesis of macroinitiators and block copolymers can be designed as shown in Scheme 1.

Isolation and Characterization of Block Copolymers

Block copolymer obtained by this way was separated from related homopolymers by fractional precipi-

tation.¹⁵ Isolated block copolymers were analyzed by spectrometric methods. For PS-*b*-PGA block copolymers, the PS amount in block copolymer was determined by measuring absorbance¹⁵ of the polymer solution in CHCl_3 at 269 nm and by comparing characteristic bands in FTIR spectra of PS-*b*-PECH, PVA-*b*-PECH, and PS-*b*-PGA block copolymers via standart calibration curves amount of polymer segments was estimated. Table I offers the results of isolation and characterization of block copolymers.

RESULTS AND DISCUSSIONS

Table I shows the results of the polymerization initiated with MI-PGA and MI-PECH. Macroinitiators were used in the bulk polymerization of styrene or VAc to obtain block copolymers having PGA and PECH units. In this manner PVAc-*b*-PGA block copolymers can also be used as liner inside of the motor case because of the better adhesive properties of PVAc. Block copolymers having PECH units were also important in the aspect of its compatibility with the vinyl polymers.

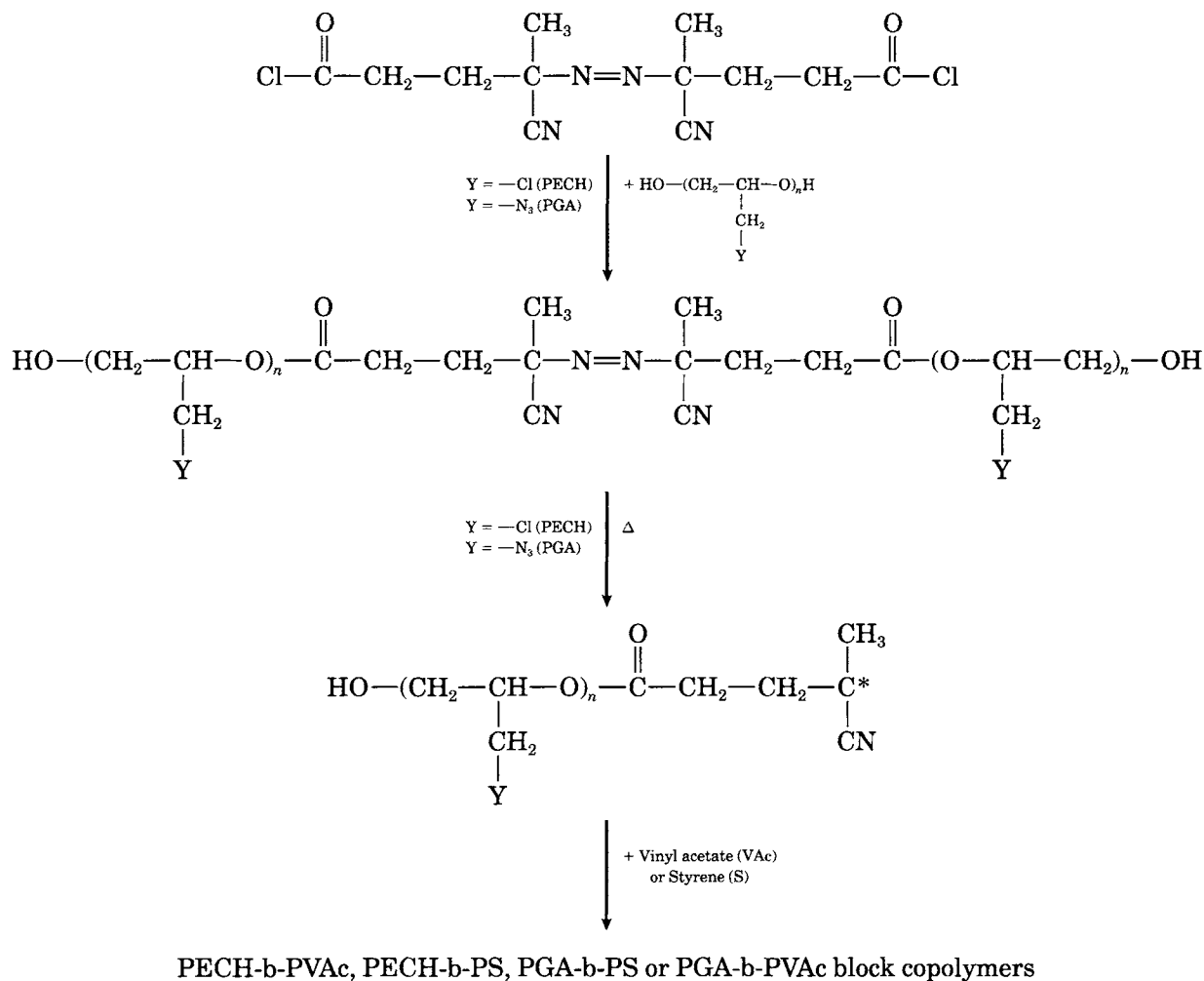
Fractional precipitation method was used to isolate block copolymers from polymerization product. γ values of the block copolymers were found between those of related homopolymers. As expected, in-

Table I Results and Conditions of the Polymerization of Vinyl Monomers with Macro-azo-initiators at 70°C

Run No.	Initiator		Monomer		M/I Ratio ^a	Polymer Time (h)	Yield of Polymer (g)	Pure Block Copolymer (%) ^b	Content of PS or PVAc Segment in Block Copolymers
	Type	Weight (g)	Type	Weight (g)					
1	MI-PGA	1.00	Styrene	5.07	5.06	3.0	2.14	73	35 PS
2	MI-PGA	2.50	Styrene	2.52	1.00	3.0	3.07	87	10 PS
3	MI-PGA	2.52	Styrene	1.02	0.41	2.0	2.61	85	5 PS
4	MI-PGA	0.92	Vinyl acetate	5.09	5.47	2.2	2.87	96	70 PVAc
5	MI-PGA	2.50	Vinyl acetate	2.53	1.01	4.0	3.32	70	19 PVAc
6	MI-PGA	2.50	Vinyl acetate	0.96	0.38	4.0	2.63	98	4 PVAc
7	MI-PECH	1.08	Styrene	4.94	4.57	4.0	2.06	98	92 PS
8	MI-PECH	2.60	Styrene	2.60	1.00	3.0	2.11	74	97 PS
9	MI-PECH	2.49	Styrene	1.17	0.47	2.2	1.70	65	70 PS
10	MI-PECH	1.06	Vinyl acetate	5.08	4.79	2.0	4.64	92	85 PVAc
11	MI-PECH	2.57	Vinyl acetate	2.68	1.04	3.0	4.56	70	40 PVAc
12	MI-PECH	2.65	Vinyl acetate	1.08	0.41	3.0	3.41	98	16 PVAc

^a Monomer-to-initiator weight ratios.

^b By fractional precipitation. Solvent: CHCl_3 ; nonsolvent: petroleum ether. γ , volume ratio of the solvent to nonsolvent: 3.5 for PS, 0.85 for PGA, 2.0 for PVAc, 1.4 for PECH; 1.5–2.5 for PS-*b*-PGA, 0.9–1.1 for PGA-*b*-PVAc, 2.4–2.8 for PS-*b*-PECH, and 1.6–1.7 for PVAc-*b*-PECH.



Scheme 1

creased macroinitiator concentration caused higher polymer yield. Consumption of VAc was also higher than that of styrene. As for the termination mechanism, at this polymerization temperature, 70°C, styrene is known to terminate via recombination exclusively, block copolymerization of styrene should produce primarily an BAB type block copolymer, while VAc might produce BA or BAB type block copolymer (B, polyether; A, vinyl polymer).

NMR and FTIR analysis of block copolymers also confirmed the presence of both polymer segments. Characteristic bands of the polymer segments in block copolymer were observed in their FTIR and NMR spectra. In the FTIR spectra of block copolymers, phenyl band of PS at 1600 cm⁻¹, C—N₃ band of PGA at 2100 cm⁻¹, C—O—C band of PECH at 1123 cm⁻¹, carbonyl band of poly(vinyl acetate) (PVAc) at 1739 cm⁻¹ were observed. In their NMR spectra, phenyl protons of PS at $\delta = 6.5\text{--}7.2$ ppm, CH₂ protons of PGA or PECH at $\delta = 3.4\text{--}3.8$ ppm and characteristic peaks of PVAc blocks at $\delta = 5.0$

and 1.8–2.1 ppm, respectively, can be observed. As typical examples, NMR spectrum of PVAc-*b*-PGA block copolymer and FTIR spectrum of PS-*b*-PECH block copolymers can be seen in Figures 3 and 4, respectively.

Thermal Analysis of Block Copolymers

Differential Scanning Calorimetry (DSC)

As a first attempt for thermal analysis of the copolymers, we determined their glass transition temperatures (T_g). In Figure 5, T_g traces of various copolymers prepared from macro-azo-initiators are depicted. For a typical block copolymer, different glass transition temperatures representing those of corresponding homopolymers can be expected. In this work, interestingly, the block copolymers showed single glass transition temperatures between T_g s of corresponding homopolymers. Figure 5(a,b) indicate T_g curves of PVAc-*b*-PGA with different

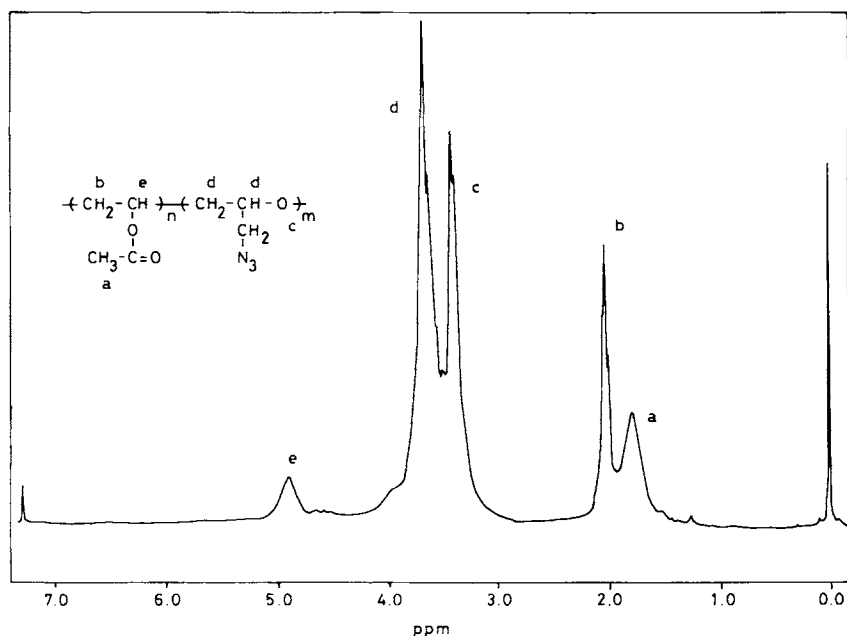


Figure 3 NMR spectrum of PVAc-*b*-PGA block copolymer (run no. 5, in Table I).

compositions. In case of a higher content of PVAc in block copolymer, the T_g value gets closer to that of PVAc. To find an explanation to this reproducible result, blends of the corresponding homopolymers were prepared and single T_g was observed, again, indicating the compatibility of the pair. Figure 5(f) and (g) show the single T_g values obtained for 1 : 1 by weight mixtures of PGA/PVAc and PECH/PVAc as -27 and -10°C , respectively, whereas T_g values are -48°C for PGA, -30°C for PECH, 110°C for PS, and 39°C for PVAc as shown in Table II. As a result, PS-PGA, PS-PECH, PVAc-PGA, and PVAc-PECH pairs are miscible. So, the pairs as in case of block copolymer or in case of blend show single T_g when they are studied in DSC.

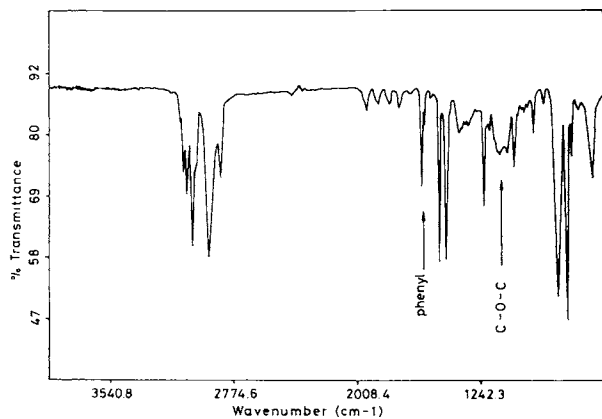


Figure 4 FT-IR spectrum of PS-*b*-PECH block copolymer (run no. 9, in Table I).

Thermogravimetry

Thermal characterization of copolymers was further achieved by recording their weight loss curves with temperature. Table II includes weight loss at the

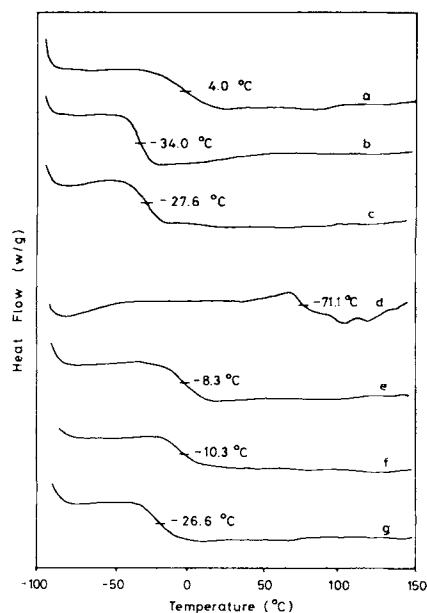


Figure 5 DSC traces of some copolymers listed in Table II: (a) PVAc-*b*-PGA (run no. 4), (b) PVAc-*b*-PGA (run no. 5), (c) PS-*b*-PGA (run no. 1), (d) PS-*b*-PECH (run no. 7), (e) PVAc-*b*-PECH (run no. 10), (f) PVAc + PECH (blend, wt ratio 1 : 1), and (g) PVAc + PGA (blend, wt ratio 1 : 1).

Table II Thermal Analysis Results of Block Copolymers Obtained by Using DSC and TGA

Run No. in Table I	Content of Vinyl Segment (Wt %)	Block Copolymer	T_g (°C)	Temperature Observed at Maximum Weight Loss Rate
1	35	PS- <i>b</i> -PGA	-27.6	248 (235), 447 (77)
4	70	PVAc- <i>b</i> -PGA	-4.0	123 (6), 255 (18), 342 (48), 477 (20)
5	19	PVAc- <i>b</i> -PGA	-34.0	121 (1), 255 (33), 340 (22)
6	4	PVAc- <i>b</i> -PGA	-42.0	254 (80), 341 (10)
7	92	PS- <i>b</i> -PECH	+71.1	130 (4), 386 (40), 420 (30)
8	97	PS- <i>b</i> -PECH	+69.0	140 (4), 371 (13), 423 (70)
9	70	PS- <i>b</i> -PECH	+58.3	121 (8), 367 (14), 423 (70)
10	85	PVAc- <i>b</i> -PECH	-8.3	106 (8), 357 (70), 456 (15)
11	40	PVAc- <i>b</i> -PECH	-22.6	105 (9), 354 (80)
12	16	PVAc- <i>b</i> -PECH	+21.6	133 (1), 351 (95)
		Homo-PGA	-48.0	255 (37), 350 (29)
		Homo-PECH	-30.0	348 (90)
		Homo-PS	+110	430 (95)
		Homo-PVAc	+39	344 (68), 460 (16)

Values are for DSC and TGA, respectively, with wt loss % in parentheses.

maxima obtained from PGA, PECH, PS, and PVAc, and their block copolymers, together with the derivative thermograms. Characteristic weight loss temperatures corresponding to the decomposition of side- N_3 chains of PGA, 252°C; subsequent decomposition of its main chain, around 340°C;¹⁷ and degradation of PS, 425°C, are clearly seen in the homo- and copolymers. When we study PVAc and those of its copolymer with three different compositions, both PGA and PVAc homopolymers show two-step thermal degradation as depicted in the derivative thermograms, whereas their copolymers again retain these behaviors and depending on the quantitative composition, with increasing PGA content, $-N_3$ elimination peak area increases (see Fig. 6).

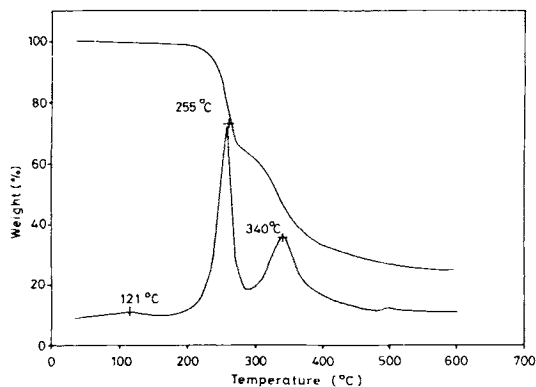


Figure 6 TGA curves of PVAc-*b*-PGA block copolymer (run no. 5 in Table II).

In case of PECH and its copolymer with PS and PVAc, PECH degrades in a single step with its maximum degradation temperature being 367°C, whereas that of PS is around 430°C. Thermal degradation of PECH/PS copolymer reflects both these behaviors and temperatures qualitatively and quantitatively. Similar effects have been observed in the case of PVAc/PECH copolymer: small shoulder on the lower temperature (around 319°C) side of the main derivative peak in Figure 7 is due to the degradation of PVAc part of the copolymer. The small peak observed in TGA traces at around 105–140°C is due to the evaporation of residual solvent/non-solvent used in the purification of copolymers or some undecomposed diazo groups of macro-initia-

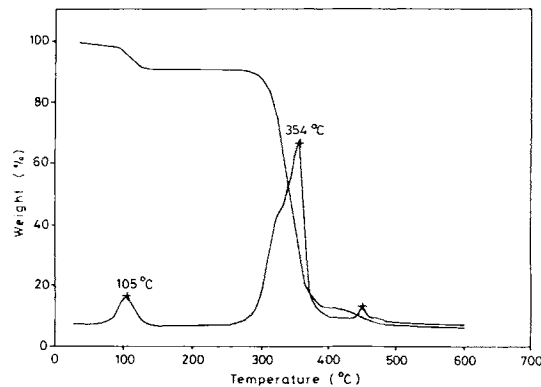


Figure 7 TGA curves of PVAc-*b*-PECH block copolymer (run no. 11 in Table II).

tors, which may be attached to the block copolymer chain.¹⁸

The dynamic thermogravimetric results obtained and discussed so far can be taken as a proof of the presence of blocks of corresponding homopolymers in the backbone. In the case of random copolymers, generally stepwise degradation of individual homopolymer segments merge into single steps located in between the maximum degradation temperatures of corresponding homopolymers. Here distinct peaks representative of thermal degradation of individual homopolymers are observed to be retained during the thermal degradation of corresponding block copolymers.

CONCLUSION

In this work, synthesis of two new macro-azo-initiators, MI-PGA and MI-PECH, by the condensation reaction of polydiols (PGA and PECH) with azobiscyanopentanoyl chloride have been reported. Block copolymerization was carried out using these macro-azo-initiators as initiator with styrene or vinyl acetate used as comonomers. Thus, block copolymers, PS-*b*-PECH, PS-*b*-PGA, PVAc-*b*-PGA, and PVAc-*b*-PECH, have been obtained. Interestingly, the results obtained from their thermal analysis showed that PGA and PECH are miscible and compatible with PS and PVAc both in block copolymer form and blends of homopolymers. Therefore, the block copolymers obtained show single T_g value between T_g values of corresponding homopolymers.

As expected, the energetic polymer, PGA, showed the lowest decomposition maximum at around 250°C among the polymers mentioned here. Additionally, it can be possible to get polyether/vinyl polymers block copolymers having different wt ratio of polyethers units by changing the feed ratio of macro-azo-initiators. In this manner, PGA-*b*-PS and

PGA-*b*-PVAc block copolymers can be used as solid rocket propellant material or energetic plastisizer with different heat capacity.

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