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SYNTHESIS AND CHARACTERIZATION OF BRANCHED
GLYCIDYL AZIDE POLYMER

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ABSTRACT

Hydroxy-terminated aliphatic polyethers having alkyl azide substituents, such as Glycidyl Azide Polymer (GAP), are useful as energetic binders in rocket propellants with reduced smoke and low vulnerability as well as in insensitive plastic bonded explosives. A novel one-step degradation process was developed for the preparation of branched GAP by reacting a solid rubbery polyepichlorohydrin (PECH) of high molecular weight ($MW \sim 10^6$) with the epichlorohydrin (ECH) monomer and sodium azide in a suitable organic solvent at 100°C for less than 15 h without a catalyst. The MW of the branched product can be controlled and predetermined in the MW range 500-40,000 by adjusting the weight ratio (ECH/PECH) in the reaction mixture. Branched GAP was characterized using different techniques such as low-angle laser light scattering (LALLS), gel permeation chromatography (GPC), viscometry, membrane osmometry, differential scanning calorimetry and bomb calorimetry. The effect of the experimental conditions on the physico-chemical properties of the branched azido product was also investigated. The degradation process yields branched GAP with a hydroxyl functionality of about 7-11 and a much lower glass transition temperature ($T_g = -65^\circ\text{C}$) and viscosity compared with linear GAP with a similar MW.

RÉSUMÉ

Les polyéthers aliphatiques à terminaisons hydroxyles ayant des substituants alkyles azidés tels que le polyazoture de glycidyle (PAG) sont utiles comme liants énergétiques dans les propergols pour fusées à fumée et vulnérabilité réduites ainsi que dans les explosifs composites insensibles. On a développé un nouveau procédé de dégradation pour la préparation du PAG ramifié en une seule étape par la réaction d'un polyépichlorohydrine (PECH) solide caoutchouteux de masse moléculaire élevée ($MM \sim 10^6$) avec le monomère épichlorohydrine (ECH) et l'azoture de sodium dans un solvant organique convenable à 100°C en moins de 15 h et sans catalyseur. La MM du produit ramifié peut être contrôlée et prédéterminée dans le domaine de MM entre 500 et 40,000 en ajustant la proportion en poids (ECH/PECH) dans le mélange réactionnel. On a caractérisé le PAG ramifié en utilisant différentes techniques telles que la diffusion de la lumière laser à petit angle (LALLS), la chromatographie par perméation de gel (GPC), la viscosimétrie, l'osmométrie par membrane, la calorimétrie à balayage différentiel (DSC) et la bombe calorimétrique. On a également étudié l'effet des conditions expérimentales sur les propriétés physico-chimiques du produit azido ramifié. Le procédé de dégradation produit du PAG ramifié avec une fonctionnalité en hydroxyle d'environ 7-11 mais avec une température de transition vitreuse ($T_g = -65^\circ\text{C}$) et une viscosité plus faible que le PAG linéaire de MM similaire.

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EXECUTIVE SUMMARY

The main purpose of a propellant binder is to hold together the ingredients of the energetic formulation in order to attain sustained burning and prevent the rapid combustion that produces a flash. Early binders such as waxes were replaced by nitrocellulose which was discovered in the 19th century. In the 1950s liquid inert binders were developed and were cured as polyurethanes. However, inert binders degrade the energy of the formulation and this loss of energy increases with the binder content. Energetic plasticizers were then used with inert binders to enhance the performance of the propellant by increasing the energy contributed by the binder and to allow the reduction of the viscosity of the formulation.

Recently, energetic binders have been synthesized for use in high-performance, insensitive, low-smoke rocket propellants. One such energetic binder which could appear in future rocket and plastic bonded explosives is Glycidyl Azide Polymer (GAP) which will be incorporated into new energetic formulations to replace the inert and currently used hydroxyl-terminated polybutadiene binder. GAP was considered as an attractive substitute for inert conventional binders because of its interesting properties and also because it was the first commercially available energetic binder prepared on a relatively large scale. GAP with a linear structure is currently produced in the USA by a two-step process; this linear GAP has a specific molecular weight (MW) of ~ 2000, a hydroxyl functionality below 2 and is relatively expensive.

The purpose of this study is to describe the synthesis as well as the characterization and properties of GAP with a branched structure prepared according to a novel degradation process developed and patented by DREV. This process is very cost-effective since the branched GAP product is obtained in a single step in a relatively short period of time from the degradation of a cheap commercial rubbery starting material. This versatile process also enables the variation of the MW of the product and yields branched GAP with a relatively high hydroxyl functionality and a lower viscosity and glass transition temperature compared with linear GAP with a similar MW. ICI Explosives Canada became greatly interested in this degradation process because of its low cost, versatility and the potential advantages of the branched GAP product. ICI obtained a license from Canadian Patents Development Ltd. for the commercial exploitation of the DREV invention. The transfer of technology to ICI has been initiated and they have recently obtained an R&D contract under the Defence Industrial Research (DIR) program.

NOMENCLATURE

a	the exponent in the Mark-Houwink relation
DMA	dimethyl acetamide
DMF	dimethyl formamide
DMSO	dimethyl sulfoxide
DSC	differential scanning calorimetry
ECH	epichlorohydrin
EG	ethylene glycol
f	hydroxyl functionality
GAP	glycidyl azide polymer
GPC	gel permeation chromatography
HBF ₄	fluoroboric acid
ΔH_c	heat of combustion
ΔH_f	heat of formation
IR	infrared
K	Mark-Houwink parameter in dL/g
LALLS	low-angle laser light scattering
LS	light scattering
MC	methylene chloride
M _e	hydroxyl equivalent weight
M _B , M _L	molecular weight of branched and linear GAP respectively
M _n , M _w	number and weight average molecular weight respectively
MW	molecular weight
NaN ₃	sodium azide
NMR	nuclear magnetic resonance
[OH]	hydroxyl concentration in the polymer expressed in meq/g
PECH	polyepichlorohydrin
PEG	polyethylene glycol
PS	polystyrene
SnCl ₄	tin tetrachloride
T	absolute temperature
T _g	glass transition temperature
THF	tetrahydrofuran
η , $[\eta]$	viscosity and intrinsic viscosity respectively
η_B, η_L	viscosity of branched and linear GAP respectively

1.0 INTRODUCTION

Hydroxy-terminated aliphatic polyethers having alkyl azide substituents, such as Glycidyl Azide Polymer (GAP), are useful as energetic binders in rocket propellants with reduced smoke and low vulnerability as well as in insensitive plastic bonded explosives to enhance performance, stability and safety and to improve the physico-chemical properties of the system. GAP with a linear structure can be prepared by two different methods:

1 - The first method

GAP is prepared by a two-step process developed in the USA; this process requires two distinct reactions (polymerization and azidation) and two distinct purification processes:

1st step: polymerization of the monomer epichlorohydrin (ECH) using a catalyst such as fluoroboric acid (HBF_4) or tin tetrachloride (SnCl_4) to obtain a liquid polyepichlorohydrin (PECH) prepolymer with a specific molecular weight (MW) (Ref. 1).

2nd step: Once PECH is prepared and purified, then the azidation of PECH to GAP is conducted either in an organic solvent such as dimethyl formamide (DMF) (Ref. 2), in an aqueous solvent (Refs. 3, 4) or in polyethylene oxides (Ref. 5). The azidation is again followed by another purification process.

GAP, obtained according to this process, has the same MW as the starting reactant PECH sample (Refs. 1, 5).

2 - The second method

GAP is prepared in a single-step process directly from the monomer ECH, without using a catalyst; the reaction is carried out at 90°C and requires less than 8 h. This process was developed at DREV

(Ref. 6) and patents were filed in Canada and the USA (Ref. 7) as well as in Europe (Ref. 8). However, this method yields GAP of low MW (approx 500) and could be used mainly as an energetic plasticizer.

A novel degradation process for the synthesis of GAP with a branched structure was developed at DREV and patents (Ref. 9) were filed in Canada, the USA, Europe and other countries. According to this process, branched GAP with a variable MW is prepared in only one step, by reacting a high MW ($\sim 10^6$) solid rubbery PECH with the ECH monomer and sodium azide in a suitable organic solvent at 100°C for less than 15 h without a catalyst. The MW of the branched GAP product can be tailored and adjusted to the desired value within a MW range of 500-40,000 by varying the proportion of the reactants. The object of this report is to describe this process as well as the characterization and properties of branched GAP prepared according to this method.

This work was performed at DREV between October 1986 and August 1989 under PSC 32C, Rockets and Missiles.

2.0 EXPERIMENTAL

2.1 The Degradation Process

GAP, with a branched structure and relatively low and variable MW, is prepared in a single step by the reaction of a very high MW solid rubbery PECH with ECH monomer and NaN_3 in a suitable organic solvent at elevated temperatures. The method of preparation of branched GAP according to the degradation process is described in the following example:

Ten g of a commercial rubbery PECH sample (MW $0.5-5 \times 10^6$) is dissolved in 50 g of dimethyl formamide (DMF) for approximately 2-6 h at 100°C with agitation. The dissolution time is dependent on the MW of the starting PECH material; high MW rubbers will generally require longer dissolution time than PECH samples with lower MW. Dimethyl sulfoxide (DMSO) and dimethyl acetamide (DMA) could also be used as solvents instead of DMF. ECH (0.25-8 g) and ethylene glycol (EG) (0.10-16 g) are then added to the mixture and the temperature is lowered to approximately 70°C . Glycerol could also be used as the initiator instead of EG. Sodium azide (8-14 g) is then gradually added to the reaction mixture in order to control the initial exothermic reaction that arises from the opening of the epoxide ring of ECH which is caused by sodium azide. This exothermic reaction proceeds for about 30 min; this "30-min" period is approximate and depends on the rate of the addition of sodium azide to the reaction mixture. The exothermic reaction is barely noticeable for low ECH concentrations but becomes more significant as the proportion of ECH is increased in the reaction mixture. The reaction is also less exothermic when carried out under a nitrogen atmosphere. It is preferable to heat the reaction mixture to approximately 70°C during the addition of NaN_3 in order to control the exothermic reaction. Once the addition of NaN_3 is complete and no sudden rise in temperature is observed, the reaction mixture is heated to about 100°C and the agitation is continued at this temperature for about 15 h. The reaction could also be achieved by gradually adding ECH (rather than NaN_3) to the reaction mixture. Heating and agitation are stopped and the reaction mixture is allowed to cool. The solid salts (NaCl and unreacted NaN_3) are then filtered and most of the DMF is evaporated at 50°C under vacuum. Fifty mL of methylene chloride (MC) is then added to the reaction mixture and followed by two 100-mL water extractions to remove the remaining DMF, EG and salts. Furthermore, a third extraction is carried out using 100 mL of 10% acetone/ H_2O or 10% methanol/ H_2O mixtures. The MC solution is dried over magnesium sulfate and then is passed through a column

containing 5 g of silica gel. The resulting solution is heated to 50°C to remove the MC and then dried under vacuum to yield the GAP product: a viscous liquid with an amber color and a density of 1.3 g/mL.

The MW of the GAP product can be controlled and adjusted to the desired value by varying the relative proportions of the reactants (ECH/PECH/ NaN_3). The weight ratio $\text{NaN}_3/(\text{ECH}+\text{PECH})$ was maintained at about 0.8 in the reaction mixture. The MW of branched GAP is lowered by increasing the weight ratio (ECH/PECH) as will be shown in Section 3.4.

2.2 GAP Characterization

2.2.1 Azide Conversion

The GAP product was characterized by NMR and elemental analysis. The azide conversion was determined by ^{13}C NMR according to the method described in Ref. 10. The elemental analysis of branched GAP with a Perkin-Elmer (model 2400 CHNO) instrument yielded: C(37.0), H(5.0), N(42.0), O(16.0) wt%.

2.2.2 Light Scattering

The Light Scattering (LS) technique was used for the determination of the M_w (weight average MW) of the polymer samples. Light Scattering measurements were performed with a KMX-6 low-angle laser light scattering (LALLS) photometer at 633 nm and an annulus of 6-7°. Details about the instrument, the method of measurement and the calculations are given in Refs. 11 and 12. The samples were characterized at 25°C in ethyl acetate and the solutions were filtered with Millipore FG membranes (porosity 0.2 μm).

2.2.3 Membrane Osmometry

Membrane osmometry was used for the determination of the M_n (number average MW) of polymer samples with relatively high MW (above 20,000). Osmotic pressure measurements were carried out in ethyl acetate at 25°C with a Hewlett-Packard, model 501 high-speed membrane osmometer using Schleicher and Schuell type membranes of regenerated cellulose with a pore size of 5 nm. Details about the instrument and the method of measurement are given in Ref. 13.

2.2.4 Gel Permeation Chromatography

The chromatograph used was a Waters (model 244A) instrument operating at room temperature using THF as a solvent with a flow rate of 1.0 mL/min. Seven ultrastyrigel columns were used with median porosities of: (1) 10⁵Å, (1) 10⁴Å, (1) 10³Å, (2) 500Å and (2) 100Å.

A Waters refractive index detector (model 401) was used. Data were analyzed by a Waters data module (model 730). All the solutions were filtered through Gelman Versapor membranes (0.2 µm) prior to injection.

2.2.5 Viscosity

The intrinsic viscosity $[\eta]$ measurements were carried out at 25°C in THF using an Ubbelohde viscosimeter. The absolute viscosity (η) measurements were determined at different temperatures using a Haake Rotovisko Rotational Viscometer. Branched GAP had a Newtonian behavior: its viscosity did not vary with shear rate.

The following empirical relation was established for branched GAP for the variation of η as a function of temperature (T):

$$\frac{d \log \eta}{d(1/T)} = 2.86 \times 10^3 \text{ cP.K}$$

2.2.6 Hydroxyl Functionality

The hydroxyl functionality (f) of branched GAP was calculated from the ratio (M_n/M_e). Three different techniques for the determination of the hydroxyl equivalent weight (M_e) were investigated:

- 1) The standard acetylation method used for hydroxy-terminated prepolymers and described in Ref. 14.
- 2) The infrared absorption spectroscopy method reported in Refs. 15 and 16.
- 3) The proton NMR spectroscopy method reported in Ref. 17.

The M_e value of branched GAP determined by acetylation was in agreement with the value obtained by IR. However, the NMR technique yielded relatively higher values for M_e for branched GAP compared to the acetylation and IR methods; the reason for this is currently being investigated. Consequently, the values of M_e reported in this document for branched GAP were determined by the acetylation and/or the IR techniques.

2.2.7 Calorimetry

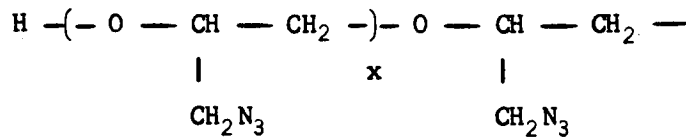
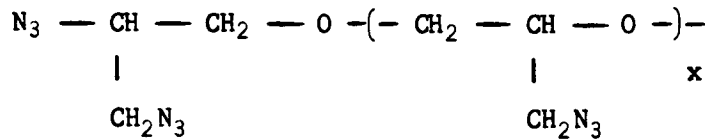
The glass transition temperature (T_g) values for branched GAP were determined with a Perkin-Elmer Differential Scanning Calorimeter (model DSC-2) at a heating rate of 20 Kmin^{-1} . The heat of combustion was determined with a Parr Adiabatic Oxygen Bomb Calorimeter (model 1241); the calculations were carried out according to the usual procedure described in Ref. 18.

3.0 RESULTS AND DISCUSSION

3.1 Degradation Mechanism

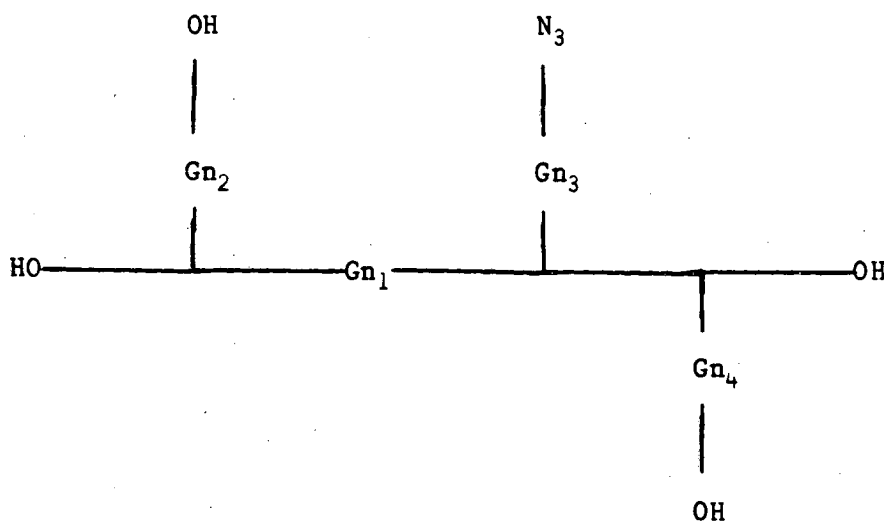
The reaction mechanism is believed to involve:

- a) The degradation and azidation of the high MW rubbery PECH, accomplished simultaneously by the sodium azide and heat. The degradation probably occurs at the oxygen bonds.
- b) The polymerization and azidation of ECH are carried out simultaneously by the sodium azide and heat according to the single-step process (Ref. 7) to yield short growing chains of low MW (~500) GAP. Two types of GAP chains with different terminal groups are obtained. Some growing GAP chains are hydroxy-terminated while others have terminal CHN_3 groups as reported in Ref. 6:



- c) These short growing chains of GAP thus formed are then grafted to the degraded rubbery matrix via chain transfer and give rise to termination and branching reactions. The grafting takes place at the oxygen bonds and probably also at the alkyl groups involved in the nucleophilic substitution.

The branched GAP product thus obtained contains OH and some N_3 terminal groups and has the following structural formula:



G = GAP unit ($-\text{CH}_2 - \text{CH} - \text{O} -$)



n = total degree of polymerization

(total number of GAP units)

$$n = (n_1 + n_2 + n_3 + n_4 + \dots + n_s) = \sum_{i=1}^s n_i$$

$5 < n < 400$,

and a molecular weight of 500 to 40,000.

n_1 = number of GAP units in segment 1

n_2 = number of GAP units in segment 2

n_s = number of GAP units in segment s

s = total number of segments in the molecule.

3.2 Molecular Weight Determination

The MW of branched GAP was determined by different techniques. The values of $[\eta]$ measured for some high MW branched GAP samples are listed in Table I along with the values of M_w and M_n determined by LALLS, membrane osmometry and GPC.

By combining the intrinsic viscosity and LALLS results reported in Table I, the following Mark-Houwink relation was established for branched GAP in THF:

$$[\eta] = 6.73 \times 10^{-4} M_w^{0.54} \quad (1)$$

The fact that the exponent in the Mark-Houwink relation has a value close to 0.50 in a good solvent is an indication of branched structure for the GAP prepared according to the degradation process.

Gel Permeation Chromatography was also used to determine the MW and MW distribution of branched GAP. The GPC calibration was performed with polystyrene (PS) standards by plotting log MW versus elution volume as shown in Fig 1. The conversion from PS MW to GAP MW was done as reported in Ref. 12 by combining the hydrodynamic volume $[[\eta] M_w]$ concept (Ref. 19) with the Mark-Houwink relation $[\eta]=KM_w^a$.

The Mark-Houwink relation reported in the literature (Ref. 20) for PS in THF is:

$$[\eta] = 9.1 \times 10^{-5} M_w^{0.746} \quad (2)$$

TABLE I

Solution properties of high MW branched GAP

Sample*	$[\eta]_{\text{THF}}$ dL/g	M_w LALLS	M_n OSMO	GPC	
				M_w	M_n
V21	0.32	97,000	36,000	85,000	32,000
V23	0.27	62,000	25,000	58,000	26,000
V25	0.24	53,000	20,000	50,000	22,000
V32	0.20	41,000		42,000	19,000
V40	0.15	25,000		27,000	15,000

* The GAP samples were obtained from the degradation of PECH Hydrin 100 in DMF for 15 h at 100°C.

TABLE II

Effect of starting material

Reactant PECH				*GAP product					
Sample	M_w LALLS	M_n Osomo	$(\frac{M_w}{M_n})$	Sample	ECH %	M_w LALLS	M_n Osomo	M_w GPC	M_n GPC
Aldrich	760,000			A33	0	53,000		115,000	37,000
				A37	30			1,800	1,600
Polyscience	1.10×10^6	118,000	9.3	V14	0	80,000	19,000	170,000	50,000
				V6	30			2,600	2,200
Hydrin H75 (B.F. Goodrich)	2.0×10^6			A31	0	100,000		210,000	68,000
				A35	30			3,200	2,600
Hydrin 100 (B.F. Goodrich)	2.85×10^6	318,000	9.0	V16	0	130,000	51,000	265,000	105,000
				H38	30			4,000	3,100

* All GAP samples were obtained in DMF after 15 h at 100°C.

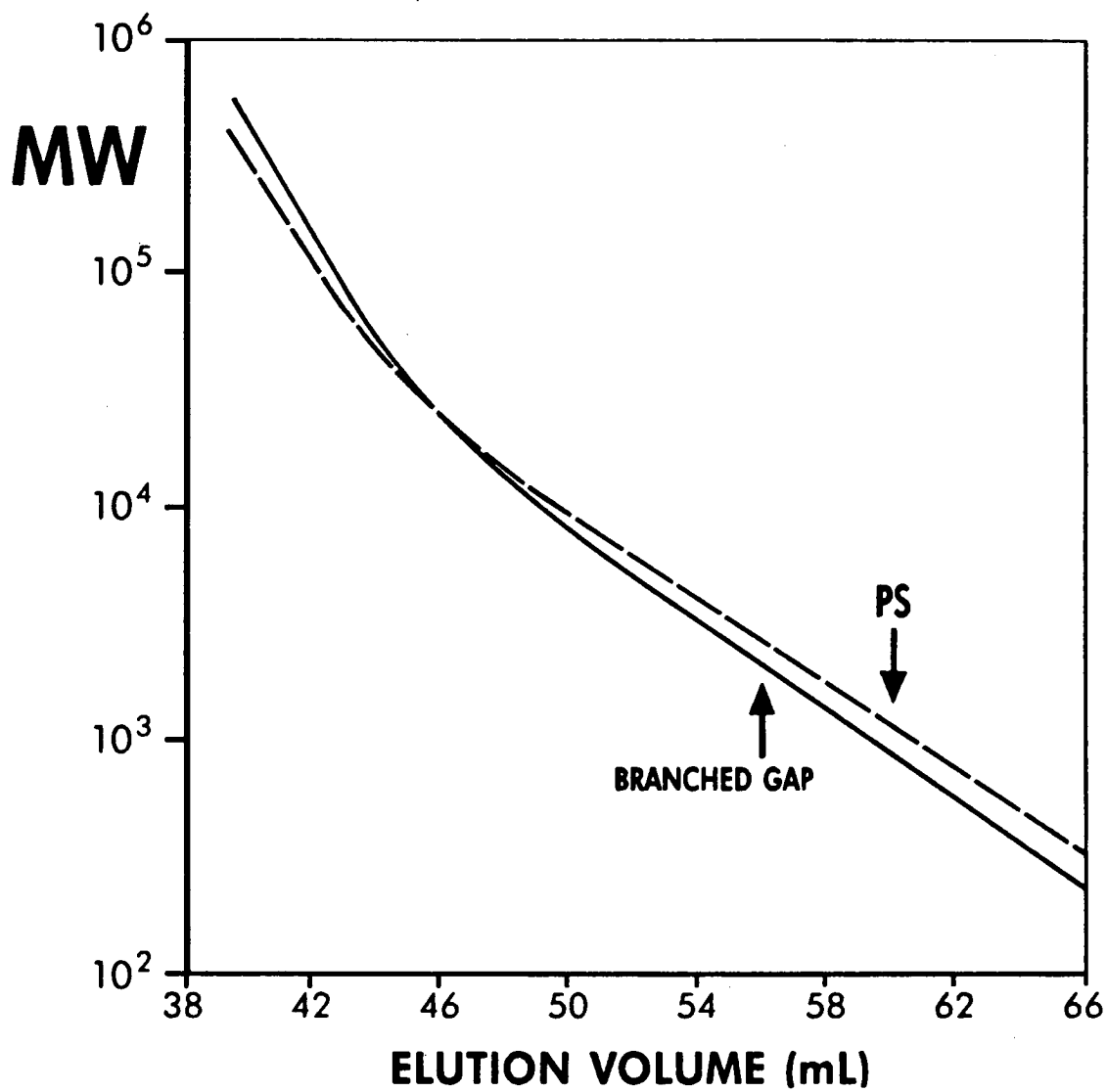


FIGURE 1 - GPC calibration curves

For a given elution volume, both PS and GAP have the same hydrodynamic volume $[\eta]M_w$; by combining the Mark-Houwink equations (1) and (2) for branched GAP and PS respectively, the following relation is obtained:

$$M_{GAP} = 0.273 M_{PS}^{1.134} \quad (3)$$

Therefore, by using eq. 3, the PS calibration curve could easily be transposed to give the calibration curve for branched GAP shown in Fig. 1. The MW averages determined by GPC for branched GAP were computed from this calibration curve. The values of M_w and M_n obtained from GPC listed in Table I are reasonably close to those determined by LALLS and membrane osmometry. This is a clear indication of the validity of the GPC calibration method.

3.3 The Starting Material

The rubbery PECH samples used in this study and obtained from different suppliers are listed in Table II. These commercial samples had M_w values ranging between 760,000 and 2.85×10^6 with a relatively high MW distribution ($M_w/M_n \sim 9.0$).

The MW of some GAP samples produced from the degradation of these PECH rubbers at ECH concentrations of 0 and 30% are also reported in Table II. The percentage of ECH is the weight fraction of monomer relative to PECH. These results were obtained in DMF for a reaction time of 15 h at 100°C. As shown in Table II, there is a correlation between the MW of the starting PECH material and the MW of the GAP product for a given ECH concentration. High MW reactant PECH samples will yield GAP products with relatively higher molecular weights compared to those produced from the degradation of low MW PECH samples. The MW of GAP sample H38 ($M_w = 4000$) produced from the

degradation of PECH Hydrin 100 ($M_w = 2.85 \times 10^6$) was relatively higher than the MW of GAP sample A37 ($M_w = 1800$) obtained from PECH Aldrich ($M_w = 760,000$) using a similar ECH concentration (ECH = 30%).

The MW of the GAP samples produced without a monomer (ECH = 0%) are much higher than those prepared with the monomer. The use of ECH in the reaction considerably reduced the MW of the GAP products; the effect of ECH concentration will be discussed in more detail in the next section. The MW averages determined by GPC for the GAP samples (A33, V14, A31, V16) prepared without a monomer were not in agreement with the absolute values of M_w (LALLS) and M_n (Osmometry) reported in Table II for these samples. The GPC calibration established for branched GAP is consequently not valid for the GAP samples produced without a monomer. Since the GPC calibration is structure dependent, the degradation of PECH without ECH yields GAP products with a structure different from those obtained with ECH. This is an indication that the branching occurs mainly from the grafting of the growing chains of GAP originating from the simultaneous polymerization and azidation of ECH.

3.4 Properties of Branched GAP

The properties of some branched GAP samples prepared at different ECH concentrations are listed in Table III. The GAP samples were obtained from the degradation of PECH Hydrin 100 in DMF for 15 h at 100°C. As shown in Table III, the values of M_w , M_n and M_e are reduced by increasing ECH%. The samples have a relatively narrow MW distribution: the ratio (M_w/M_n) is equal to 1.2 ± 0.1 . A typical GPC chromatogram for branched GAP is shown in Fig. 2 for sample V58: a sharp and nearly symmetrical main peak with some tailing containing

TABLE III

Properties of branched GAP

Sample*	ECH %	GPC			M_e	f	T_g (°C)	ΔH_c (cal/g)
		M_w	M_n	$\frac{(M_w)}{M_n}$				
V26	9	11,400	9,000	1.27	820	11.0	-51	-4,995
V58	13	8,300	6,500	1.28	770	8.4	-55	-5,025
V59	20	5,500	4,200	1.31	540	7.8	-55	-5,000
V75	26	4,500	3,600	1.25	470	7.7	-60	-5,010
C05	33	3,300	2,700	1.22	390	6.9	-60	
M33	44	2,300	2,000	1.15	260	7.7	-65	

* The GAP samples were obtained from the degradation of PECH Hydrin 100 in DMF for 15 h at 100°C.

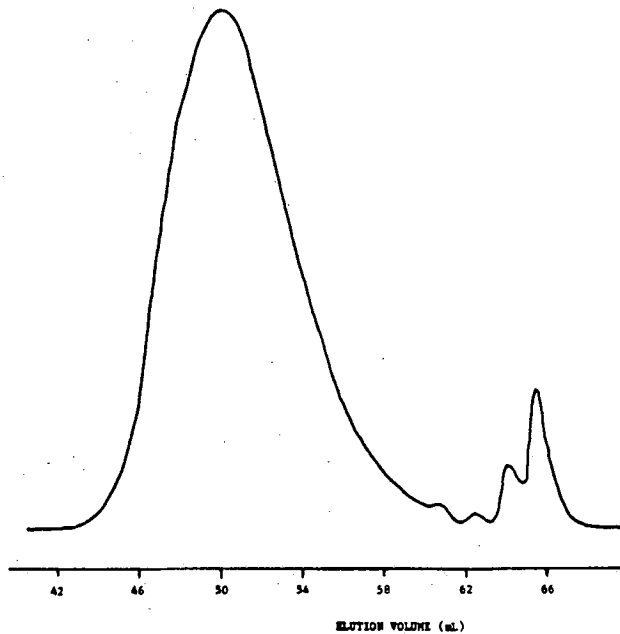


FIGURE 2 - GPC chromatogram of sample V58

shoulders and small humps towards the low MW end, corresponding to GAP oligomers. The variations of M_w and $[\text{OH}]$ versus ECH% are also plotted in Fig. 3. $[\text{OH}]$ expressed in meq OH/g, is the hydroxyl content of the polymer and is equal to $(1000/M_e)$. Figure 3 shows that the MW of branched GAP can be controlled and predetermined by adjusting the monomer concentration in the reaction mixture (i.e. for a given PECH, solvent, reaction temperature and sequence of addition of the reactants). Figure 3 also shows that the hydroxyl content of branched GAP increases with ECH%. This is an indication that most of the OH groups are incorporated into the molecule by the grafting of GAP chains originating from the simultaneous polymerization and azidation of the ECH monomer.

As shown in Table III, the hydroxyl functionality is relatively high ($f = 6.9 - 11.0$); this is an indication that GAP obtained from the degradation process has a branched structure with mostly OH terminal groups. By way of comparison, the value of f determined for linear GAP was equal to 1.5 (Ref. 12).

The values of T_g reported in Table III decrease when the MW is lowered as expected. As a low T_g is usually an indication of superior physico-chemical properties for the binder, the degradation process enables the production of branched GAP of variable and relatively high MW but with still a lower T_g compared to linear GAP. As shown in Table III, sample V75 with $M_w = 4500$ has a T_g of -60°C compared to a T_g of -55°C for linear GAP of MW 2000 (Ref. 12).

The heats of combustion (ΔH_c) for some branched GAP samples are listed in Table III; ΔH_c is essentially constant (-5010 ± 15 cal/g) in the MW range investigated. An endothermic value of 42 kcal/mol was calculated for the heat of formation (ΔH_f) of branched GAP from the value found for ΔH_c and according to the following equation:

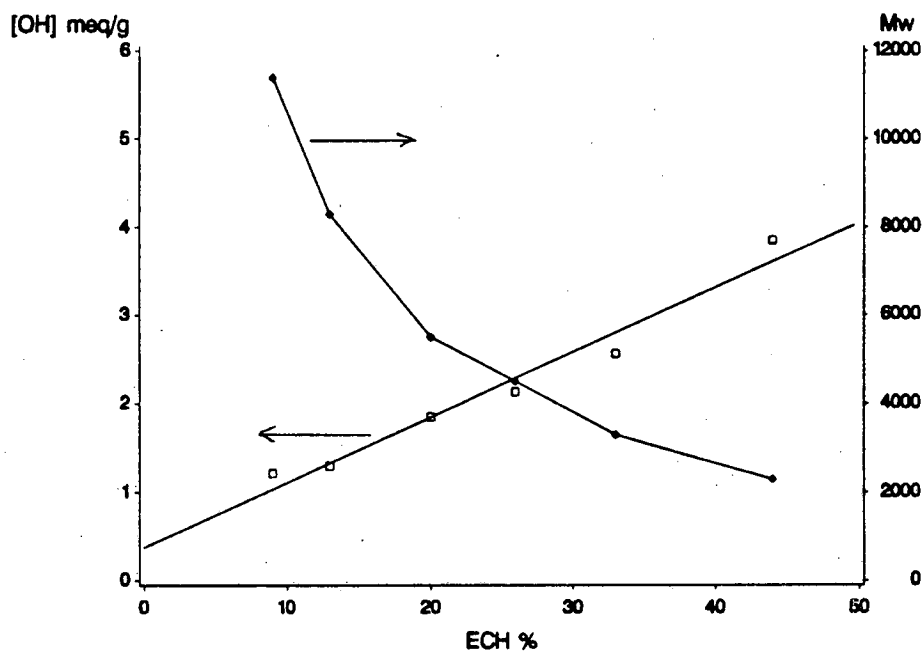
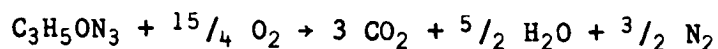


FIGURE 3 - Variation of M_w and $[OH]$ with ECH concentration

TABLE IV

Viscosity - Molecular weight relationship

GAP	Sample	$\eta_{25^\circ\text{C}}$ cP	M_w GPC
BRANCHED	A19	2,000	1,900
	C17	5,000	4,000
	A15	7,900	5,400
	M32	12,600	10,000
	V62	50,000	22,000
	X07	79,000	37,000
LINEAR	100-14	450	560
	200-7A	4,600	1,920



In comparison, the value determined for ΔH_f of linear GAP was 28.4 kcal/mol (Ref. 12). This is important from the standpoint of propellant formulations since the specific impulse of a propellant is proportional to $(\Delta H_f)^{1/2}$ of the reactants. The relatively higher values found for ΔH_f of branched GAP could be attributed to the presence of some terminal azide groups in the molecular structure as mentioned in Section 3.1.

3.5 The Viscosity - Molecular Weight Relationship

The values of η and M_w determined for some branched GAP samples as well as two linear GAP samples obtained from Rockwell are listed in Table IV. A graph of $\log M_w$ versus $\log \eta$ is also plotted in Fig. 4 for branched and linear GAP. As shown in the graph, branched GAP has a higher MW than linear GAP with a similar viscosity. Consequently, the viscosity of branched GAP will be generally lower than that of linear GAP with a similar MW. This is another indication of the branched structure of GAP prepared according to the degradation process. As the MW decreases, the curve for branched GAP approaches the linear GAP curve and finally meets it at a MW of about 200 which corresponds to a GAP dimer. The following η - M_w relationships were calculated from the two curves drawn in Fig. 4, corresponding to branched and linear GAP:

$$\log M_B = 1.05 + 0.70 \log \eta_B \quad (4)$$

$$\log M_L = 1.36 + 0.52 \log \eta_L \quad (5)$$

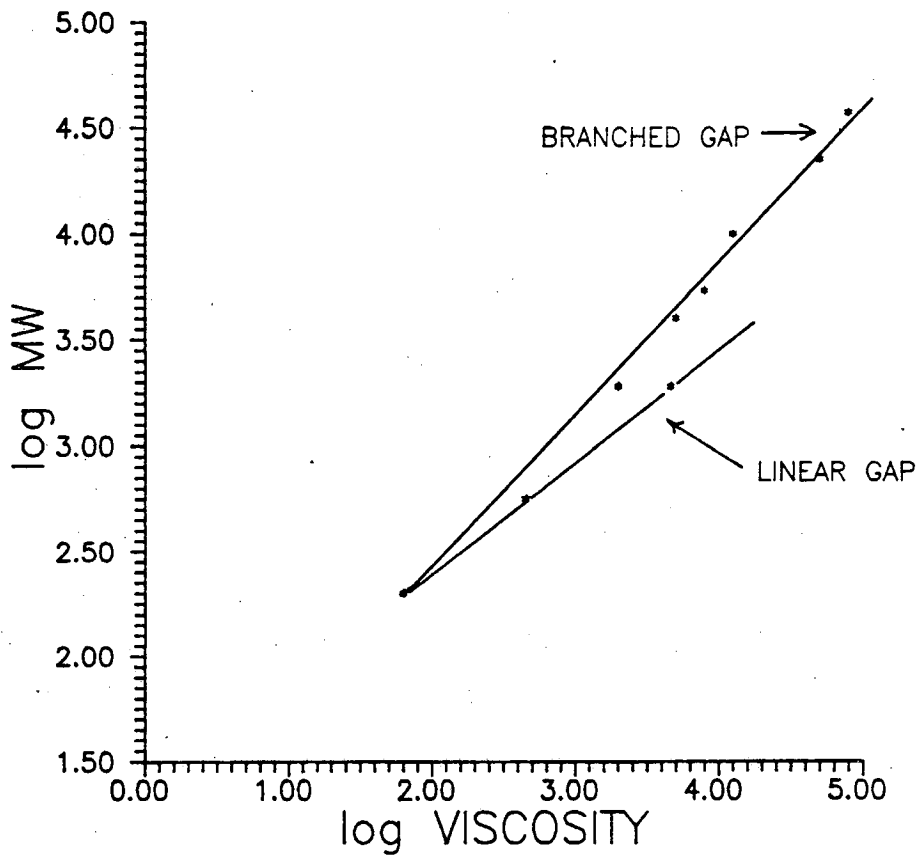


FIGURE 4 - Viscosity - molecular weight relationship

TABLE V

Molecular weight of branched versus linear GAP

$\eta_{25^\circ\text{C}}$ cP	M_L	M_B	$\frac{M_B}{M_L}$
4,000	1,800	3,800	2.1
10,000	2,900	7,200	2.5

η_B and η_L are the viscosity of branched and linear GAP respectively. M_B and M_L are respectively the MW of branched and linear GAP. By combining eqs. 4 and 5, the following empirical relation was established between the MW of branched and linear GAP polymers for a given viscosity:

$$M_B = 0.17 M_L^{1.336} \quad (6)$$

Since viscosity is an important factor in the processing of binder formulations, the degradation process enables the production of higher MW branched GAP in the viscosity range (4000-10,000 cP) normally used in the processing of linear GAP of lower MW as shown in Table V. Consequently, the degradation process enables the use of higher MW binders in rocket propellants and plastic bonded explosives while maintaining the viscosity at sufficiently low levels so as not to hinder processing.

3.6 Effect of Reaction Solvent

The solvent employed in the degradation process must dissolve the rubbery PECH and also partially dissolve the NaN_3 in order to accomplish both the degradation and azidation reactions. The effects of different solvents on the azide conversion and the MW of the GAP product are reported in Table VI. Polar organic solvents such as DMF, DMA, DMSO and dioxane were tested; butyl acetate and polyethylene glycol (PEG) of MW 400 were also investigated as solvents.

As shown in Table VI, total azidation was accomplished after only 15 h in DMF, DMA and DMSO. However, for a similar concentration of monomer (ECH = 20%) and initiator (EG/solvent = 0.06), the GAP product (sample V46) obtained in DMSO had the highest MW (8500), whereas the GAP sample (A07) produced in DMF had the lowest MW (5500).

TABLE VI

Degradation of PECH Hydrin 100 at 100°C in different solvents

Solvent	Sample	ECH %	Reaction time (h)	($\frac{EG}{Solvent}$)	Azide conversion %	M _w GPC
DMF	A07	20	15	0.06	100	5,500
DMA	B20	20	15	0.06	100	6,700
DMSO	V46	20	15	0.06	100	8,500
PEG (MW400)	L25	80	30	0.67	82	1,000
Dioxane*	L32	71	40	0.08	63	100,000
Butyl acetate	L14	60	40	0.50	65	6,300
	L13	50	20	0.33	40	210,000
	L10	60	20	0.50	59	112,000
	L11	64	20	0.58	67	28,000

* For dioxane the degradation temperature was 90°C.

In PEG and butyl acetate, complete azidation was not achieved even after a longer reaction time and at relatively higher concentrations of monomer (ECH = 50-80%) and initiator (EG/solvent = 0.33-0.67). In dioxane, a relatively high MW (100,000) product (sample L32) containing 63% GAP was obtained after 40 h for ECH = 71%. In PEG, a relatively low MW (1,000) product (sample L25) containing 82% GAP was obtained after 30 h for ECH = 80%. In butyl acetate, by increasing the monomer concentration, the MW was reduced and the azide conversion was raised as indicated by the results of samples L13, L10 and L11; by doubling the reaction time, the azide conversion was not significantly increased but the MW was considerably lowered as observed for sample L14.

The best solvents for the synthesis of branched GAP are then DMF, DMA and DMSO. The other solvents investigated are not recommended since the azidation as well as the degradation are only partially accomplished even after increasing the reaction time and using excessive monomer and initiator concentrations.

3.7 Effect of Some Reaction Parameters

The effect of some reaction parameters on the MW and azide conversion of branched GAP are reported in Table VII; the samples were obtained from the degradation of PECH Hydrin 100 in DMF. The results found for samples C13 and C16 (obtained after 15 and 30 h respectively) indicate that the MW decreases with the reaction time as expected. When the reaction was carried out in two stages of 15 h each (15 h without NaN_3 followed by an azidation period of 15 h) as in the case of sample V74, the results were similar to those found for sample C16 (30 h azidation). This is an indication that, at high temperatures, DMF catalyzes the degradation reaction. No further significant reduction in the MW was observed when the reaction time was extended from 30 to 45 h; the MW values of sample M34 (obtained after 45 h with ECH=22%) are

TABLE VII

Effect of some reaction parameters on the degradation of PECH Hydrin 100 in DMF

Parameter	Sample	Reaction		ECH %	Azide conversion %	GPC		
		Temperature (°C)	Time (h)			M_w	M_n	$\frac{M_w}{M_n}$
Reaction time	C13	100	15	22	100	5,200	4,000	1.30
	C16	100	30	22	100	4,100	3,400	1.20
	V74	100	30*	22	100	4,300	3,500	1.23
	M34	100	45	22	100	4,000	3,200	1.25
Reaction temperature	V57	70	68	39	86	8,000	1,300	6.15
Monomer concentration	V51	100	15	55	100	1,200	400	3.0
Sequence of addition of reactants	L33	100	15	26	100	4,100	3,200	1.28

* 30 h (15 h without NaN_3 + 15 h with NaN_3)

close to the values reported for sample C16 obtained after 30 h with a similar ECH concentration. Since total azidation is accomplished in DMF after 15 h at 100°C and as no significant reduction in the MW was noticed after 30 h, there is no advantage in using a reaction time longer than 30 h in this solvent at this temperature.

The effect of using a lower reaction temperature was also investigated as reported in Table VII for sample V57 prepared at 70°C. The values of the M_w (8000) and the MW distribution ($M_w/M_n = 6.2$) for this sample are much higher than the results obtained in Table III for a GAP sample prepared at 100°C with a similar ECH concentration. Furthermore, the azide conversion was only 86% for sample V57 even after 68 h at 70°C. The GPC chromatogram obtained for sample V57 in Fig. 5(a) showed a broad MW distribution: a symmetrical peak at the high MW end followed by another peak with some humps and shoulders corresponding to GAP oligomers. A decrease in the reaction temperature caused a reduction in the degradation rate and thus a MW increase. Consequently, it is preferable to carry out the degradation at 100°C since a low temperature (such as 70°C) will require a much longer reaction time to achieve complete azidation and will yield a product with a relatively higher MW and MW distribution.

The effect of using an excess of monomer in the reaction was also investigated as reported in Table VII for sample V51 prepared with ECH = 55%. The GPC chromatogram obtained for sample V51 in Fig. 5(b) showed multiple peaks and the presence of a significant proportion of low MW material. This explains the relatively low value of M_n (400) found for sample V51. These results indicate that when an excessive amount of ECH is used, a fraction of the monomer does not participate in the grafting reaction but yields rather low MW (500) chains of GAP according to the single-step process (Ref. 6). The final product thus obtained is a blend comprised of branched GAP with a relatively high MW as well as linear GAP of low MW (500). This phenomenon was observed when monomer concentrations exceeding 45% were used in the reaction.

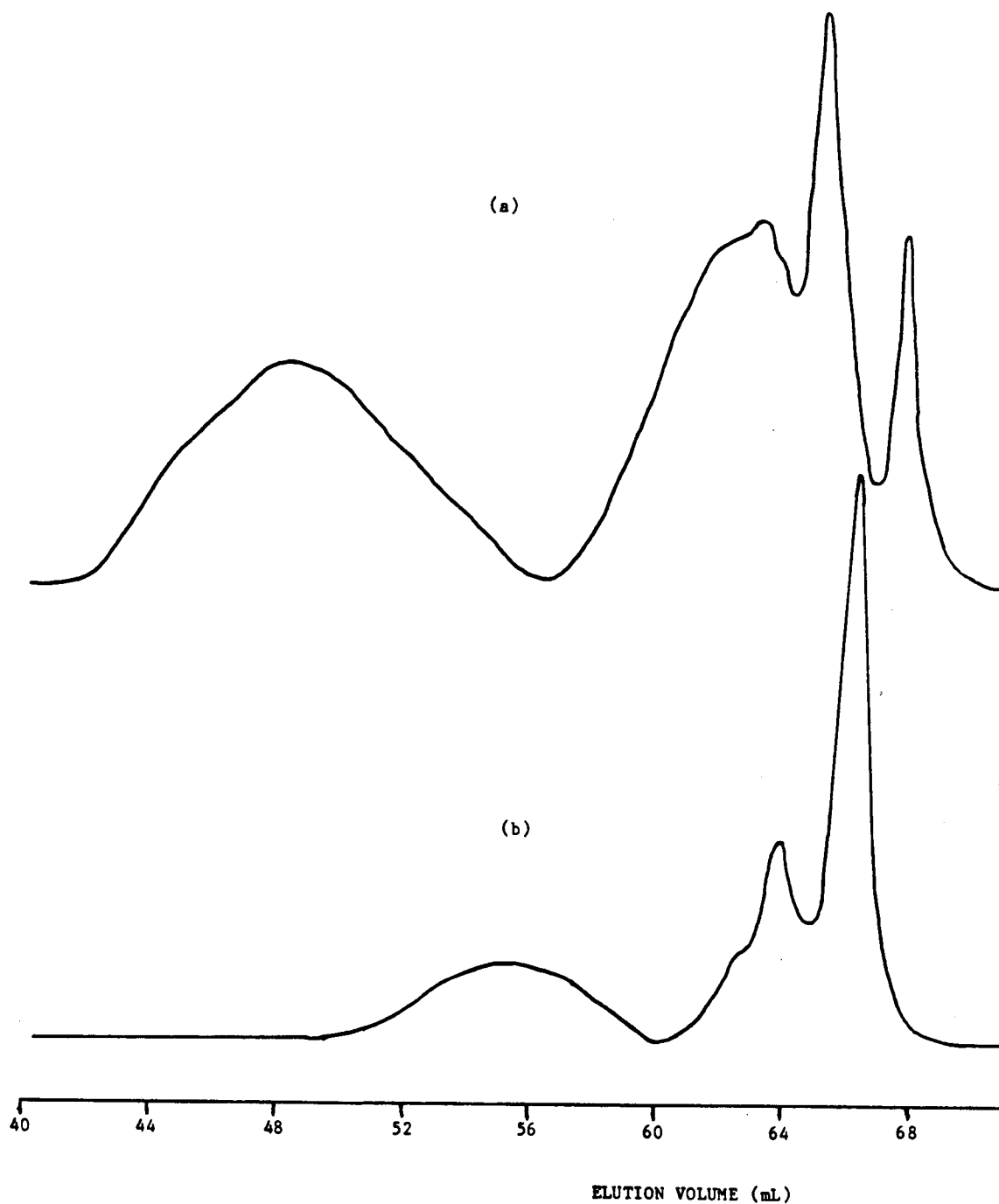


FIGURE 5 - GPC chromatograms

a) sample V57 prepared at 70°C

b) sample V51 obtained with ECH = 55%

The effect of the sequence of the addition of the reactants was also investigated as reported in Table VII for sample L33 obtained by the gradual addition of ECH (rather than NaN_3) to the reaction mixture. The MW averages found for this sample are comparable to the results listed in Table III for a GAP sample prepared at 100°C with a similar ECH concentration but prepared by gradually adding NaN_3 to the reaction mixture. However, the color of sample L33 was darker than the GAP samples listed in Table III. This phenomenon is now being investigated and will be reported later.

4.0 CONCLUSIONS

Glycidyl Azide Polymer with a branched structure and variable and predetermined MW can be prepared directly from the reaction of a solid rubbery PECH of high MW ($\sim 10^6$) with the ECH monomer and NaN_3 according to a novel degradation process developed at DREV. The synthesis of branched GAP is carried out at 100°C in DMF for about 15 h without a catalyst. The MW of branched GAP may be controlled and adjusted to the desired value in the MW range of 500-40,000 by varying the relative proportion of the ingredients in the reaction mixture. This process appears cost-effective since the reaction is accomplished in a single step in a relatively short time period and requires a cheap, commercially available rubbery PECH as the starting material.

Branched GAP has a higher hydroxyl functionality ($f = 7-11$) and heat of formation but a lower viscosity and T_g (-65°C) than linear GAP with a similar MW.

This versatile process yields GAP binders with tailored MW and M_e values; this could enable greater flexibility in the optimization of the mechanical properties of energetic formulations.

In this study, the rubbery polymer (PECH) and the epoxide monomer (ECH) were of the same type and a branched GAP homopolymer was therefore produced. The degradation process, when applied to other systems (rubber polymer/epoxide monomer), could yield different kinds of energetic homopolymers, copolymers and terpolymers with a branched structure having a predetermined relatively low MW. A study has been undertaken to prepare and characterize some copolymers based on GAP and the results will be reported later.

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