

Synthesis and Thermal Characterization of Polybutadiene Azide

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The present work presents the possibility of introducing new functional groups on the chains of polybutadiene. The polybutadiene is obtained by a radical polymerization in a solution. In an intermediate step, an addition of bromine (Br_2) is carried out. The azide group ($-\text{N}_3$) is grafted on the polybutadiene chain by a reaction of substitution with bromine under well defined conditions. The virgin and modified polymers are characterized by infrared spectroscopy, differential scanning calorimetry analysis, thermogravimetric analysis and elemental analysis. These studies confirm the existence of the grafted group and evaluation of quantify their percentages.

Key Words: Energy groups, Polybutadiene, Modification, Graft.

INTRODUCTION

Chemical modification is one of methods for obtaining materials derived from natural or synthetic polymers for which a monomer does not exist. For obtaining polymers having specific properties, the chemical modification is more commonly employed. The grafting of some chemical functions on polybutadiene constitutes a significant alternative to obtain a polymer which is of great importance, particularly in the energetic and medical fields¹. During pyrolysis or combustion processes, some groups, like the azide ($-\text{N}_3$), nitrites ($-\text{NO}_2$) and the nitramines ($-\text{N}-\text{NO}_2$), release the heat owing to the scission of their chemical bonds which are highly exothermic^{2,3}. The grafting of one of these groups on polybutadiene certainly increase these energy performances. In the last few years, new polymeric types containing the groups of azide, methyl azide and acrylates have been developed⁴⁻⁸. In the present work, we are particularly interested, to the study of the chemical modification of polybutadiene by azide group through substitution of its brominated form.

EXPERIMENTAL

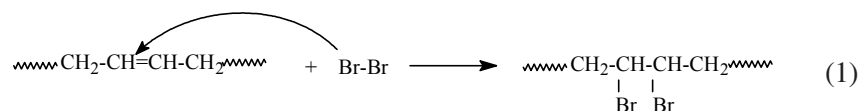
Synthesis of polybutadiene: The butadiene monomer (Merck 99 %) is used without other purification. It is condensed in double-walls graduated bulb. The solvent, tetrahydrofuran (Merck 99 %) is purified by bidistillation and is dried under sodium wire. The reactional mixture is maintained at a temperature of -10 °C using a cryogenic liquid (ethanol + water). The initiator (naphthalene-alkaline) being used is introduced into the mixture under inert atmosphere. At the end of polymerization, the solution was kept for a few minutes. The polymer formed is precipitated in methanol excess containing an antioxidant (N-phenyl-β-naphthylamine).

The polymer is precipitated two to three times in methanol and separated by filtration, then washed several times with distilled water and alcohol. It is finally vacuum dried, at a temperature of 40 °C, till constant weight and preserved in an inert atmosphere and protect from the light. The polymers obtained in the tetrahydrofuran are solids viscous, rubbery, sticky and have yellowish colour.

The polymer obtained is a mixture of three isomers which are the form *cis* (26 %), the *trans* form (34 %) and vinyl form (40 %). Its viscometric mass (*M_v*) is 2550 g/mol (obtained by capillary method). It has a glass temperature from -63 °C, determined by DSC7 Perkin Elmer with a heating rate of 10 °C/mn. Several tests of solvation were carried with the assistance of toluene, THF, benzene and *n*-hexane. The latter proved to be better solvent for the two principal reactants (polybutadiene and bromine).

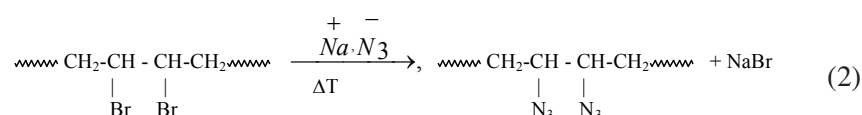
Bromination of polybutadiene: In an Erlenmeyer flask of 250 mL, 3 g of polybutadiene dissolved in 40 mL of *n*-hexane at constant temperature and pressure. The bromine solution (1.5 mL dissolved in 100 mL of hexane) is poured drop by drop in the polymeric solution under moderate agitation. The instantaneous formation of a suspension of white colour is noticed and the colour of bromine disappears at the first contact with the solution, confirming its reaction of bromination on the double bond of the polybutadiene.

The addition of two atoms of bromine on the double bond presents the character of a reaction in two stages, first step consists of an electrophile attack on the π bond electrons, the molecule of Br₂ undergoes a heterolytic rupture and the cation fragment sets the first on one of ethylene carbon, The anion then binds, thanks to the free doublet it has, on the other carbon⁹.



Addition of azide group to polybutadiene: In a 250 mL container, 2 g of brominated polybutadiene was dissolved in 100 mL of THF. A quantity of sodium azide NaN₃ (0.3 g) is added to the polymeric solution.

The mixture is maintained at a temperature of 60 °C, under a moderated agitation during 48 h. The formed precipitate (NaBr) is purified and filtrated. The filtrate is subjected to a reduced heating by using a rota-vapour. The polymer is then recovered in the form of a film after the total evaporation of solvent. This reaction is a nucleophilic substitution of the bromine by the group (-N₃), coming from the sodium azide (NaN₃).



Characterization: Polybutadienes, brominated polybutadienes and azide were characterized by infrared spectroscopy using standard Shimadzu type 8400s in the range 4000-400 cm⁻¹. Table-1 carries the key absorption bands characteristic of pure and substituted polybutadiene.

TABLE-1
KEY IR BANDS (cm⁻¹) OF POLYBUTADIENES
AND SUBSTITUTED POLYBUTADIENES

Polymer	Frequency (cm ⁻¹)	Vibrations
Pure polybutadiene	3075	=CH Elongation
	1640	C=C Elongation
	995	C-H Angular vibration in the plane
	970	C-H Angular vibration of the <i>trans</i> form
	910	C-H Deformation out of plane
Brominated polybutadiene	670	C-H Deformation of the <i>cis</i> form
	1065	C-H Elongation of carbon brominated
	600	C-Br Deformation in the plane
Polybutadiene azide	550	C-Br Deformation out of plane
	3390	C-H Elongation of carbon azide
	2135	C-N ₃ Elongation

The spectrum of pure polybutadiene is characterized in particular by types of vibration of valence average intensities of the bond (=CH) of 3075 cm⁻¹ and C=C of 1640 cm⁻¹ and by strong deformation intensity of the C-H bond, in and out of the plane, respectively with 995 and 910 cm⁻¹, of a deformation of the C-H bond (*trans*) of strong intensity to 970 cm⁻¹ and in end of deformation of low intensity of the C-H bond (*cis* form) at 670 cm⁻¹. The absorption spectra of brominated polybutadiene, in addition to the absorption bands existing in the case of pure polybutadiene, transitions from deformation and in particular for the strong intensity C-H bond (1065 cm⁻¹) of the brominated carbon are observed. For C-Br, two bonds of low intensities are located, in and out of the plan at 600 and 550 cm⁻¹, respectively.

Concerning the spectrum polybutadiene azide, the polybutadiene-Br transitions disappear to appear under a wide bond with low intensity at 3390 cm^{-1} and a strong peak at 2134 cm^{-1} characterizing the elongations of the bonds C-H of carbon azide and C-N₃, respectively. In addition to the characterization by FTIR, the pure polybutadiene and polybutadiene azide were subjected to the elemental analysis.

TABLE-2
ELEMENTAL ANALYSIS OF POLYBUTADIENE AND
POLYBUTADIENE AZIDE

	Elemental analysis (%)			Residual (%)
	C	H	N	
Pure polybutadiene (PB)	65.50	8.60	0.00	25.90
Polybutadiene azide (PB-N ₃)	32.80	5.20	22.00	40.00

The residual percentage (% residual), translates the mass of the polymerization igniter, existing at the ends of the polymeric chain. Samples of 10 mg of polybutadiene and PB-N₃ were subjected to a differential scanning calorimeter (DSC7, Perkin-elmer) in the temperature range 50 to 500 °C, with a heating rate of 10 °C/min.

The thermogram presented in Fig. 1 shows a single clear exothermic and rapid peak at 395 °C for pure polybutadiene. On the other hand, for polybutadiene azide, the exothermic peak is moved to 345 °C. This peak has an area definitely higher than that of pure polybutadiene (Fig. 2). The area of the exothermic peak is directly connected with the calorific potential of each polymer. The peak area ratio (polybutadiene-N₃)/peak area (polybutadiene) is estimated to 5.

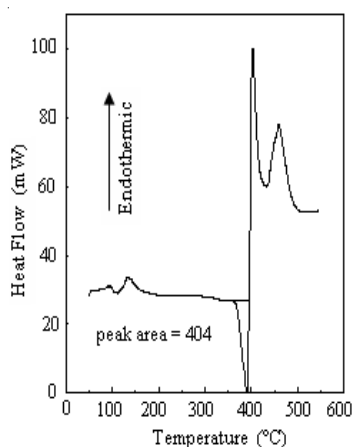


Fig. 1. Thermogram DSC of pure polybutadiene

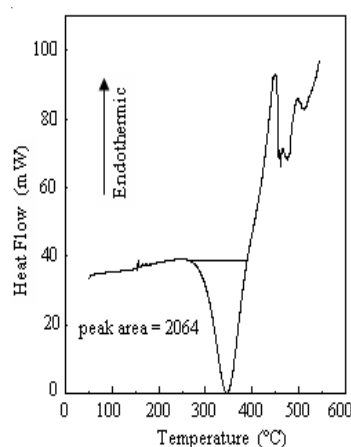


Fig. 2. Thermogram DSC of polybutadiene-azide

For better understanding the nature of these transitions, two samples, respectively, pure polybutadiene and PB-N₃, were subjected to thermogravimetric analysis, using a standard Setaram thermobalance (precision 10⁻⁸) with a heating rate of 10 °C/min and under a primary vacuum (10⁻² torr).

According to the thermogram of pure polybutadiene (Fig. 3) a total mass loss was observed in the vicinity of 400 °C. On the other hand, on the thermogram of polybutadiene azide (Fig. 4), shows two different stages of mass loss. The first appears at 389 °C is attributed to chain grafted azide and the second at 408 °C.

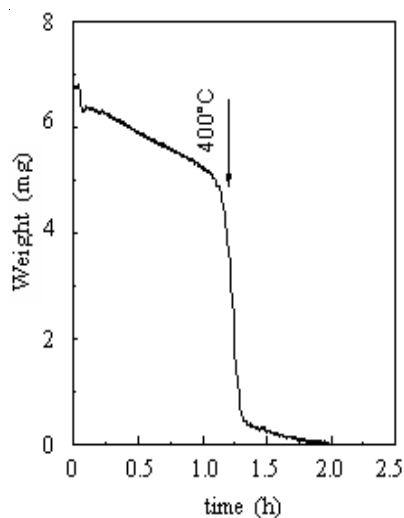


Fig. 3. Thermogram of pure polybutadiene

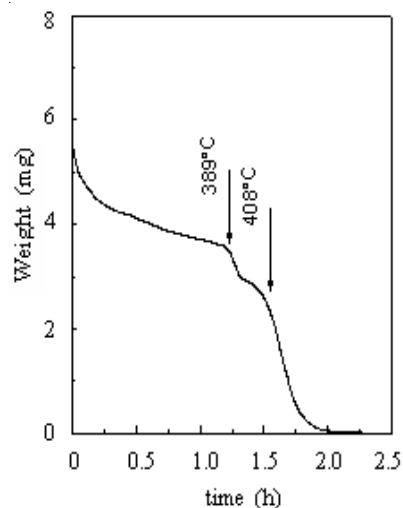


Fig. 4. Thermogram of polybutadiene-azide

It is clear that polybutadiene-azide has a thermal behaviour different from that of pure polybutadiene. The loss of mass with time is attributed to the decomposition of the polymer. This degradation (loss of mass) which generally follows a complex mechanism is characterized by cuts of chains leading to simple molecules.

Conclusion

This study enabled us to modify the structure of polybutadiene and to reach an appreciable rate of grafting (22 %) in azide group (-N₃). The examination of the FTIR spectra highlighted the presence of this group on the chain of polybutadiene.

In addition the exploitation of the thermal analysis the DSC and TGA showed that polybutadiene-azide degrades first, but less quickly than pure polybutadiene not modified.

By comparison of the exothermic peaks, polybutadiene-azide is five times more energetic than pure polybutadiene.

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