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Synthesis and characterization of (deuterated) polybutadienes of well-defined molecular weight and microstructure

Laurent Joguet, Rachel Mansencal, Bassel Haidiar, Alain Vidal (✉), Philippe Dumas

Institut de Chimie des Surfaces et Interfaces – CNRS, B.P. 2488, 68057 Mulhouse, France
e-mail: A.Vidal@univ-mulhouse.fr, Fax: +33 3 89 60 87 99

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Summary

In order to attain reliable information on the structuration and organization of macromolecules participating to interphases in multicomponent materials, it is necessary to use polymers of well defined characteristics in terms of molecular weight, molecular weight distribution and microstructure. This paper describes the synthesis and characterization of a series of polybutadienes, using deuterated monomers in particular. The obtaining of the latter from 2,5-dihydrothiophene-1,1-dioxide and their subsequent polymerization will be described together with some of the characteristics of the resulting polymers.

Introduction

Use of well defined macromolecular chains (molecular weight, microstructure,...) is a prerequisite to be in a position to assess the characteristics of filler/elastomer interphases. This applies particularly when the latter are examined through their conformational and dynamic properties using for example solid state NMR techniques. In this respect deuterated polymer chains are of a particular interest [1,2]. We describe in this paper the synthesis and characterization of a series of polybutadienes of either identical molecular weight and variable microstructure or identical microstructure and variable molecular weight. A particular emphasis will be placed on the synthesis of deuterated materials, which involved two steps, first the preparation of the labeled monomer which was selectively [3-6] deuterated, then its polymerization.

Experimental

Reagents

1,3-butadiene (Fluka, puriss.) was, before use, either dried over molecular sieve (4 Å) or purified in the reaction flask by use of sec-butyllithium (Aldrich). 1,3-butadiene (1,1,4,4-D_4) was synthesized from 2,5-dihydrothiophene-1,1-dioxide (Fluka, purum) using deuterium oxide (Cambridge Isotope Laboratories Inc., D > 99.9 %) for isotopic exchange. Either N,N,N',N'-tetramethylethylenediamine or bis-piperidinoethane

(Fluka, molecular biology grade) were used for obtaining polybutadienes of the desired microstructure, they were used as received. Prior to use, all solvents (toluene, dioxane) were twice distilled and dried over sodium for 10 days.

Instruments

Polymerizations were performed either in a pressure proof reactor or under high vacuum in a glass apparatus connected to a vacuum line.

Size exclusion chromatography (SEC) analyses were performed on a Waters 150C ALC/GPC equipment, using Hibar Lichrogel columns (PS400, PS40, PS10; Merck), differential refractomer and UV absorption detector, with tetrahydrofuran as the carrier solvent (1 ml/min). Calibration was conducted with polystyrene standards.

Glass transition temperatures were measured over the – 150 °C to + 200 °C temperature range (temperature increment: 10 °C/min), using a Mettler DSC30 equipment.

Polymer microstructure was determined from ^{1}H (Bruker AC 250, QNP probe) and ^{13}C liquid NMR spectra (Bruker ARX 300).

Synthesis of 1,3-butadiene (1,1,4,4-D$_4$)

Preparation of deuterated sulfone: The deuterated sulfone was obtained according to the procedure developed by Cope, Berchtold and Ross [6]. In a typical experiment, 0.847 mol (100 g) of 2,5-dihydrothiophene-1,1-dioxide (powder) was dispersed, in presence of 1 g potassium carbonate (catalyst), in a solution of deuterium oxide (100 g, 5 mol) in 50 ml of previously dried dioxane. The isotopic exchange, performed at room temperature under strong stirring for three days, was followed by the recovery and drying of the sulfone. In order to improve the yield of the isotopic exchange process the operation was repeated 3 times. After an ultimate drying step and purification by dissolution in excess dioxane, the deuterated sulfone was freeze-dried so as to get rid of any remaining deuterium oxide or dioxane. The sulfone (white solid, m.p. ~ 70 °C) was recovered with an 80 % (w/w) yield. Deuteration ratios deduced from liquid NMR spectra indicated a yield of the isotopic exchange process in excess of 90 %.

Obtaining of 1,3-butadiene (1,1,4,4-D$_4$): It resulted from the thermal decomposition of the deuterated sulfone [6]. 100 g of the latter, placed in a round-bottom flask equipped with a temperature probe and a nitrogen inlet, were heated under nitrogen flushing to 130-150 °C. Sulfur dioxide formed was absorbed by passing the gas flow through a series of 3 traps containing respectively 20 and 40 % aqueous potassium hydroxide solutions and potassium hydroxide pellets intermixed with Raschig rings. 1,3-butadiene (1,1,4,4-D$_4$) was collected in a trap cooled with liquid nitrogen. When gas release was over, the trap containing the condensed butadiene was allowed to warm to room temperature and the monomer was stored in a freezer over dibutyl magnesium so as to obtain a reactant free of any trace of water at the ppm scale. The yield was 85 % of the theoretical amount.

Polymerization

Synthesis of polybutadienes with variable 1,2- content: Butadiene was anionically polymerized according to the procedures of Halasa et al. [7] and Sänger et al. [8] playing on the amount of bis-piperidinoethane (BPE, stereospecific additive) and the temperature (from 6 to 40 °C) to obtain the desired microstructure. Besides the above-mentioned parameters, all syntheses were performed under the same experimental conditions, i.e. for 50 g predried butadiene, cyclohexane (300 ml) was used as a solvent, and sec-butyl lithium (s-BuLi, 1.1 mol/l) as initiator, 4,5-methylenephenantrene (MPT) being used as a color indicator for the titration of protic impurities (concentration adapted to that of BPE in order to have an unambiguous coloration of the reaction medium). After 24 hours, the polymerization was quenched by addition of isopropanol and the polymer precipitated in excess methanol in presence of a few drops of 2,6-di-tert-butyl-4-methyl phenol in order to protect the polybutadiene from any oxidation. After filtration and drying in a vacuum oven at room temperature, the polymer was stored at low temperature (0 °C) up to its utilization.

Synthesis of D-polybutadienes: The procedure used for the anionic polymerization of 1,3-butadiene (1,1,4,4-D_4) was the same as the previous one, beside the use of toluene as a solvent in order to obtain a polymer which is mainly 1,4- in microstructure. In a typical experiment, after carefully drying the vacuum apparatus and vacuum line through a series of thermal treatments and nitrogen flushing, 100 ml purified toluene (twice distilled, dried for ten days over sodium) was added to 12 g deuterated butadiene, followed by 2 ml s-BuLi together with MPT used as a color indicator. The temperature of the reaction bath was first set at -70 °C then slowly increased up to 30 °C, temperature at which the polymerization was performed. After 24 hours, the reaction was quenched by addition of 10 ml ethanol and the polymer was treated as previously described.

Characterization of the obtained polybutadienes

Determination of their molecular weight and molecular weight distribution, assessment of their microstructure and evaluation of their thermal properties characterized the obtained polybutadienes.

Polybutadienes with variable microstructure

Table I provides the experimental conditions retained for the obtaining of materials of well-defined structure ranging from 10 to 100 % 1,2-PB contents and the microstructure of the corresponding materials. The relative proportions in 1,2- and 1,4-PB are deduced from the ^{1}H NMR lines located at 4.95 ppm (1,2-PB =CH2) and 5.40 ppm (1,4-PB =CH), respectively. The results obtained point at the obtaining of materials the 1,2-PB contents of which is in agreement with the expected values. The precise microstructure of the synthesized polymers was deduced from the intensity of the ^{13}C peaks associated with the aliphatic carbons of the cis (27.5 ppm) and trans (32.7 ppm) 1,4-PB, respectively. One can check that both BPE concentration and temperature control the microstructure of the polybutadiene samples. Use of increasing proportions of BPE favors high 1,2-PB contents, while an increase of polymerization temperature at constant BPE concentration results in a depletion of the

1,2-PB moiety. In absence of BPE, high 1,4-PB proportions (91 %) are attained.

Table I Experimental conditions retained for the synthesis of polybutadienes with variable 1,2-contents. Microstructure of the corresponding samples

Expected 1,2-PB (%W)	MPT (mmol)	BPE (µmol)	T (°C)	Microstructure (%W ± 1.0)		
				1,2-PB	cis 1,4-PB	trans 1,4-PB
10	0.234	0	40	9.0	40.9	50.1
20	0.188	26	50	16.5	36.5	47.0
30	0.184	40	40	31.0	26.8	42.2
40	0.156	60	45	41.5	21.3	37.2
50	0.184	80	45	51.5	18.6	29.9
60	0.156	100	40	63.5	11.1	25.4
70	0.156	80	25	74.6	9.9	15.5
80	0.156	100	25	80.2	7.6	12.2
90	0.078	500	25	95.0	0.8	4.2
100	0.156	1000	6	96.4	1.5	2.1

Figure 1 provides the evolution of the glass transition temperature and the heat capacity change of the synthesized polybuadienes vs. their 1,2-PB contents. The T_g of the corresponding samples increases linearly with their 1,2-PB ratio. The extrapolated

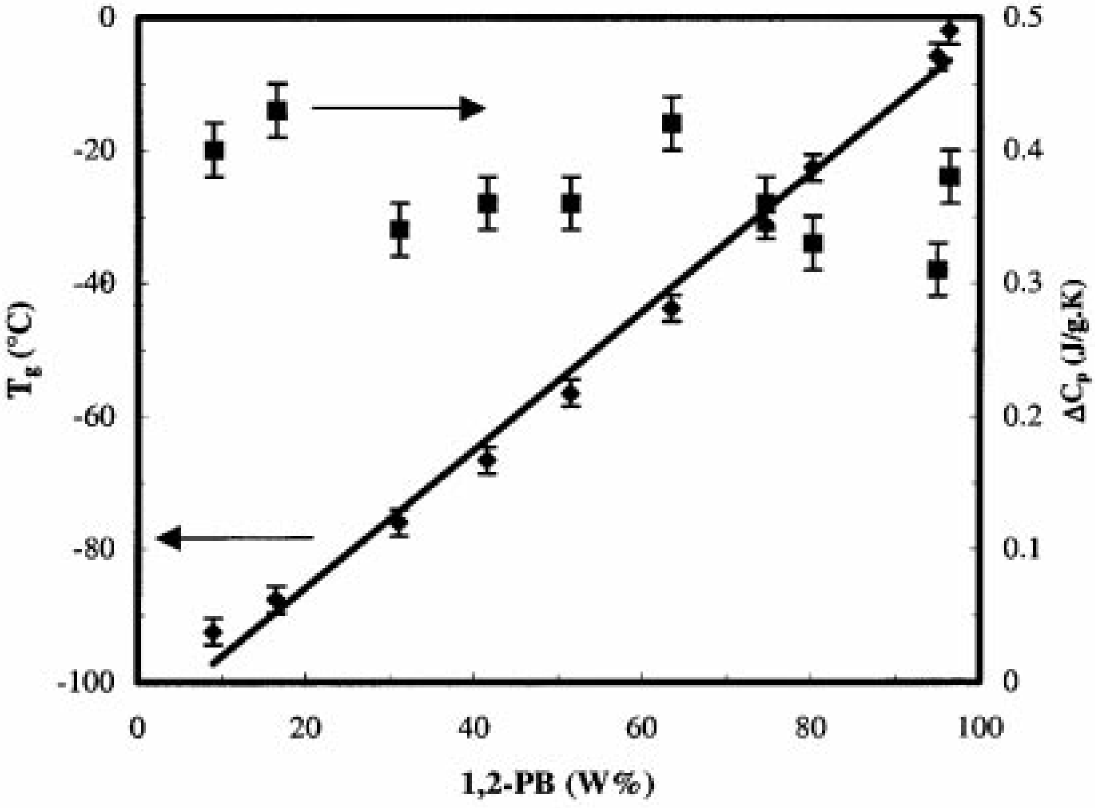

Fig. 1 Evolution of the thermal characteristics of the synthesized polybutadienes with their 1,2-PB contents (◆ : T_g; ■ : ΔC_p)

T_g's of pure 1,2- and 1,4-PB obtained by linear regression, i.e. - 2°C and - 110°C respectively, are in agreement with the values reported in the literature [9]. As for the ΔC_p's, this thermodynamic parameter appears to be independent, within the experimental error, on the microstructure of the polymer.

The molecular weights and molecular weight distributions of the different samples as calculated from SEC measurements using PS standards are reported as M_w and M_n polystyrene equivalents (PSeq) in Table II. They are also provided as absolute values (M_n) after correction of the previous values using factors obtained by comparison of data yielded by GPC on the one hand and osmometry on the other hand. These adjustment factors are equal to 0.77 and 0.65 for 100 % and 8 % 1,2-PB samples, respectively [10]. They change linearly with the 1,2-PB content of the samples. The corrected M_n's appear to be quite constant for the whole range of samples prepared. The molecular weight distribution of the different polymers is also very much identical.

Table II Average PS equivalent (PSeq) molecular weights, corrected M_n's and molecular weight distributions

1,2-PB (%W)	M_{wPSeq}	M_{nPSeq}	M_n	M_{wPSeq}/M_{nPSeq} (± 0.1)
9.0	196000	176000	114000	1.1
16.5	182000	162000	107000	1.1
31.0	189000	168000	114000	1.1
41.5	198000	176000	122000	1.1
51.5	173000	158000	111900	1.1
63.5	167000	152000	110000	1.1
74.6	174000	161000	119000	1.1
80.2	134000	124000	93000	1.1
95.0	157000	147000	112000	1.1
96.4	169000	154000	118000	1.1

D-polybutadienes

Using ^1H and ^{13}C NMR to control the microstructure of the deuterated polybutadiene, it appears that the ^1H line located at 4.95 ppm (1,2-PB $=CH_2$) is barely detectable, which confirms the use of a monomer that is fully deuterated at the 1 and 4 positions.

Table III Main characteristics of the deuterated polybutadienes

M_{nPSeq} (g/mol)	M_{wPSeq}/M_{nPSeq} (± 0.1)	T_g (± 2°C)	Microstructure (%W ± 0.1) 1,2-PB	cis 1,4-PB	trans 1,4-PB
2750	1.1	- 96	10	35	55
8500	1.1	- 90	14	29	57
11000	1.2	- 89	12	31	57
25800	1.1	- 90	12	42	46
49300	1.1	- 89	16	46	38
67000	1.1	- 89	14	32	54

Table III provides the main characteristics of the obtained polymers. One may check that they cover a large domain of molecular weights but are rather monodisperse and have fairly constant 1,2-PB contents. The attainment of this well-defined microstructure is confirmed by the T_g value of the different samples, which are quite similar and in good agreement with the values obtained for the nondeuterated polybutadienes (figure 1).

Conclusion

The anionic synthesis of nondeuterated and partially deuterated polybutadienes with defined characteristics (microstructure, molecular weights and molecular weight distributions) was described. In this respect we particularly prepared well-characterized deuterated materials. After compounding with reinforcing fillers (carbon blacks, silicas) these compounds will be used in a further step to attain information on the structuration and organization of macromolecules participating to interphases in multicomponent materials.

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