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Synthesis of *N*,*N*-diethyldithiocarbamate functionalized 1,4-polyisoprene, from natural rubber and synthetic 1,4-polyisoprene

D. Derouet [a,*], Q.N. Tran [a,b], H. Ha Thuc [b]

[a] *L.C.O.M. Chimie des Polymères (UMR du CNRS UCO2M N°6011), Université du Maine, Faculté des Sciences, Avenue Olivier Messiaen, 72085 Le Mans Cedex 9, France*

[b] *Laboratoire des Polymères, Université des Sciences Naturelles d'Ho Chi Minh Ville, Département de Chimie-Physique, 227 rue Nguyen Van Cu, 5ème Arrondissement, Ho Chi Minh Ville, Viet Nam*

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Abstract

N,*N*-Diethyldithiocarbamate functionnalized 1,4-polyisoprenes were prepared from 1,4-polyisoprenes (natural or synthetic). The syntheses were performed by nucleophilic addition of *N*,*N*-diethyldithiocarbamate salts upon oxirane rings of epoxidized units according to a SN2 mechanism with ring opening. Studies on model molecules of epoxidized 1,4-polyisoprene units (1,2-epoxy-1-methylcyclohexane and 4,5-epoxy-4-methyloctane) were previously achieved to develop the procedure. The best yields were obtained at low temperature in polar medium, and more especially in water with sodium *N*,*N*-diethyldithiocarbamate (DEDT-Na) as reagent. A diastereospecific addition was noted when reaction was performed in water with DEDT-Na. Afterwards, the developed procedure was successfully generalized to epoxidized synthetic polyisoprenes and epoxidized natural rubber (in THF, then in latex medium). Excellent results were obtained in latex medium with epoxidized natural rubber (ENR) latices. As with the models, a diastereospecific addition of sodium *N*,*N*-diethyldithiocarbamate trihydrate onto epoxidized 1,4-polyisoprene units of ENR was observed at the condition to bring the latex medium to pH 8 before introduction of DEDT-Na. Influence of temperature, drc, and DEDT-Na concentration were successively examined to determine the best conditions of the addition on ENR latices.

Keywords: Iniferter; Natural rubber; Polyisoprene; Chemical modification; Latex; *N*,*N*-Diethyldithiocarbamate

1. Introduction

1,4-Polyisoprene rubbers (natural or synthetic) have commercial interest (elasticity, electric insulation…) required for special applications as elastomeric material in various industrial sectors (tyres, adhesives, housing…). In efforts to extend their use, various chemical and physical methods were

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[*] Corresponding author. Tel.: +33 0 243833326; fax: +33 0 243833754.
E-mail address: Daniel.Derouet@univ-lemans.fr (D. Derouet).

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developed to modify their properties [1–5]. These modifications are not only directed towards the enhancement of certain properties characteristic of the respective polyisoprenes, but also to introduce totally new properties not usually associated with these rubbers, or to transform them into new products used as high added-value for special applications. In particular, the method was extensively applied to polyisoprene rubbers, natural or synthetic, to prepare various new interesting rubbery materials such as photocrosslinkable [6], antioxidizing [7], flame resistant [8], and thermoplastic NR [9] rubbers. Two chemical strategies are commonly developed to prepare these polymers: by direct addition of electrophilic reagents onto carbon–carbon double bonds of the rubber chains or addition of nucleophilic reagents onto epoxidized units previously created on the polyisoprene backbone. The latter solution is of great interest because the oxirane groups of he epoxidized units can easily react in mild conditions with a large scale of nucleophilic reagents such as acids, amines, and alcohols [10]. Unlike most ethers, oxiranes react easily with many strongly nucleophilic reagents. These reactions are not different from the nucleophilic displacements, except that the leaving group, the oxygen of the epoxide ring, remains a part of the original molecule.

The grafting of *N*,*N*-diethyldithiocarbamate groups onto polyisoprene rubbers was not reported until now, probably owing to the absence of an available procedure for carrying the reaction. Indeed, no method was described to introduce this type of function onto trisubstituted carbon–carbon double bonds, and yet, this should present some interest because of the well known extensive use of organic compounds containing dithiocarbamate groups primarily as accelerators for sulfur vulcanization of rubbers [2,11], as fungicides and bactericides [12], as drug against alcoholism [13], but also as initiators for radical photopolymerization of vinyl monomers. They can be applied for the synthesis of block and graft copolymers [14–16]. For instance, under UV irradiation, a polymer chain having a dithiocarbamate group is dissociated and generates two radicals: one is a polymeric radical and the other is a relatively stable dithiocarbamate radical. During the polymerization, the dithiocarbamate radical caps the growing radical reversibly.

The objective of the present paper is to relate the syntheses developed to prepare *N*,*N*-diethyldithiocarbamate functionalized 1,4-polyisoprenes, our intention being to prepare thermoplastic-grafted polyisoprene by photopolymerization of vinyl monomers initiated from a rubber backbone according to the principle of "grafting from". For that, the grafting of *N*,*N*-diethyldithiocarbamate functions in side position of 1,4-polyisoprene chains (natural or synthetic) was envisaged by a two-step process. In the first step, the purpose was to create reactive functions along the rubber chains to be used as reactive sites able to be substituted, during the second step, by *N*,*N*-dialkyldithiocarbamate carbanions according to a nucleophilic substitution mechanism. A preliminary study on model molecules of 1,4-polyisoprene units (1-methylcyclohexene, 4-methyloct-4-ene) was performed to determine the best conditions of the synthesis, but also to collect spectroscopic information useful for the characterization of the *N*,*N*-diethyldithiocarbamate functionalized 1,4-polyisoprenes.

2. Experimental

2.1. Materials

Solvents used as eluent in high performance liquid chromatography were of analytical grade and used as received. Dichloromethane, acetone, methanol, diethyl ether were purified according to the classical methods. THF was distilled on sodium-benzophenone under argon atmosphere, then stored over 4 Å molecular sieves.

Tert-amyl alcohol ($Eb_{760\ mmHg} = 102$ °C, Janssen), *n*-butyl bromide ($Eb_{760\ mmHg} = 103$ °C, Janssen Chimica), and 2-pentanone ($Eb_{760\ mmHg} = 101$ °C, Janssen Chimica) were distilled before use.

Diethylammonium *N*,*N*-diethyldithiocarbamate (DEDT-DA) (Aldrich), sodium *N*,*N*-diethyldithiocarbamate trihydrate (DEDT-Na) (Acros), 1-methylcyclohexene (Fluka), tetraethylammonium bromide (TEAB) (Acros), tetrabutylammonium bromide (TBAB) (Acros), triphenylphosphine (Janssen) were used as-received. 4-Methyloct-4-ene was prepared by Wittig–Schölkopf reaction between *n*-butylidenetriphenylphosphorane and 2-pentanone [17].

The reagents used for the epoxidations, *m*-chloroperbenzoic acid (Aldrich), hydrogen peroxide (35 weight percentage in water, Acros), and formic acid (Acros) were used as-received.

Natural rubber latex (42% drc, origin: Thailand), synthetic liquid polyisoprene (LIR-30: ($\overline{Mn} = 15,000 g\,mol^{-1}$), $I_p = 1.5$) (Siber Hegner), and