

Synthesis of small molar mass perdeuterated polyethylpropylene (d-PEP) as an auxiliary for neutron studies

Frederik C. Krebs*, Mikkel Jørgensen, Bente Lebech, Kristoffer Almdal, Walther B. Pedersen

Condensed Matter Physics and Chemistry Department, Macromolecular Chemistry, Risø National Laboratory, P.O. Box 49, DK-4000 Roskilde, Denmark

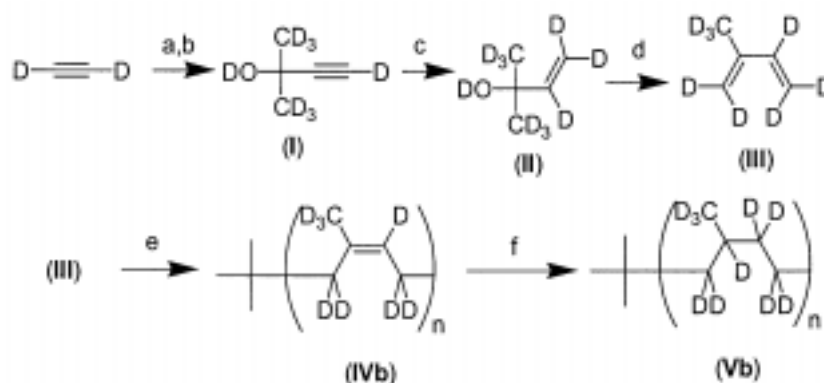
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Summary

An inert non-crystalline cryoprotectant oil was needed as a non-incoherent scattering matrix for neutron studies of solvent containing crystalline materials. This led us to prepare perdeuterated polyethylpropylene (PEP) with a molar mass around 1100 g/mol. On route to this material an improved method for the preparation of isoprene-d₈ starting from calcium carbide and acetone-d₆ was devised. Subsequent anionic polymerization using t-butyl lithium as initiator resulted in an oligomeric perdeuterated polyisoprene (PI) with an average chain length of approx. 15 monomer units and Mw/Mn: 1.1. This polymer was deuterated with D₂ and Pd/C (10%) in cyclohexane to yield the desired perdeutero polymer (PEP-d). The polymer fulfill the important properties that it does not crystallize at low temperature and has a low neutron scattering efficiency.

Introduction

Low molar mass oils are used as inert matrices in X-ray crystallography to handle sensitive crystals that may otherwise rapidly loose solvent of crystallization and thereby disintegrate. A similar oil was needed for neutron studies. The oil should be reasonably viscous at ambient temperature so that it completely covers and protects the crystalline material while it is handled. This also slows diffusion of any solvent from the crystals into the oil. The neutron studies are performed at liquid nitrogen or helium temperatures where the oil should become a glass and not contain crystalline domains. An extra requirement however, is that the oil does not contain significant amounts of hydrogen that scatters incoherently and gives rise to a high background. These requirements led us to consider a small molar mass and fully deuterated PEP for this use. Isoprene-d₈ has been prepared previously (1) in good yield and in large quantities, but using tedious exchange reactions and cumbersome workup procedures. An improved synthesis was therefore developed which is outlined in the scheme.



Scheme. a: n-BuLi, b: acetone-d₆, c: D₂ Pd/C, d: Al₂O₃ Δ, e: t-BuLi, f: D₂ Pd/C.

* Corresponding author

Deuterated polyisoprene (d-PI) has been prepared for studies of polymer blends (3,4) or for small angle neutron scattering studies of the polymer itself (5). The polymer with the remaining double bonds deuterated (d-PEP) has been reported (6,7,8).

Experimental

Newtonian viscosity measurements were carried out on a RMS 800 rheometer from Rheometrics. Size Exclusion Chromatography (SEC) was carried out on a Viscotec Differential Refractometer/Viscometer using a Jordi 100 Å column and THF as eluent using a Shimadzu LC-10AD pump set at 1.00 mL/min. The calibration curve was established by means of low molar mass PI standards from Polymer Laboratories, UK. MALDI-TOF mass spectra were recorded on a HP-G2025A instrument. ¹H, ²H and ¹³C NMR spectra were recorded on a Bruker 250 DPX instrument at 250.1, 38.4 and 62.9 MHz respectively. All solvents were HPLC grade except for THF which was distilled from sodium benzophenone ketyl.

Synthesis

1) 2-methyl-but-3-yn-2-ol-d₈ (**I**)

4 L of acetylene-d₂ was generated by dropwise addition of 7 mL D₂O to 22 g of powdered CaC₂. The gas was transferred to a volumetric cylinder (4 L) displacing water. The acetylene-d₂ gas was dried through CaCl₂ and bubbled into 1.8 L dry THF cooled to -78 °C on a dry ice acetone bath. This procedure was repeated eight times until a total of 32 L acetylene-d₂ had been absorbed in the 1.8 L THF. Mono lithio-acetylide-d was prepared by adding 600 mL 1.6 M *n*-BuLi in hexanes carefully keeping the temperature below -70 °C to avoid generation of di-lithio acetylide. The slightly yellow turbid solution was stirred for 10 min. after which 75 mL acetone-d₆ was added keeping the temperature below -70 °C. After stirring for 15 min at this temperature the cooling bath was removed and the reaction mixture left overnight. 40 mL of D₂O was added slowly while stirring. The mixture became thick and after about 30 min the precipitate was filtered and washed twice with 250 mL pentane. The combined organic phase was distilled through a 30 cm column packed with Raschig rings. The fraction at 103-5 °C was collected and redistilled to give a colorless liquid. Yield: 63.9 g (72 %, based on *n*-BuLi).

2) 2-Methyl-but-3-en-2-ol-d₁₀ (**II**).

Lindlar catalyst (1.51 g) was placed in a stainless steel bomb hydrogenation apparatus with a system volume of 700 mL and evacuated. 67.8 g of (**I**) in 50 g pentane was introduced via a syringe. The system was pressurized to 33 Bar with D₂. The system became warm and the reaction was finished in 10 min. After cooling to ambient temperature the reaction mixture was filtered through Celite, washed with pentane and the combined organic phases were distilled through a packed column. 50 mL of decane was added to the distilling flask to allow complete recovery. The fraction boiling at 96-8 °C were collected. Yield (77%).

3) Isoprene-d₈ (**III**).

Compound (**II**) (54 g) was pyrolysed according to the literature procedure (1). Yield 36 g (97 %)

4) PI-h (**IVa**).

Cyclohexane 100 mL and 35 g isoprene (0.513 mol) was stirred at ambient temperature under argon while 17 mL 1.5 M t-BuLi was added rapidly over 1 min. The mixture was heated to 38 °C where the reaction commenced. A temperature of 50 °C were maintained over 2 hrs. after which water (50 mL) was added. The organic phase was separated, dried and evaporated to give a clear oil. Yield: 32.7 g (90 %). SEC showed that the Mw was 1760 g/mol in good agreement with the Mw of 1741 g/mol obtained from MALDI-TOF MS.

5) PI-d (**IVb**)

36 g Isoprene-d₈ (**III**) was stirred with 10 g Al₂O₃ (neutral) for 10 min. and then distilled onto a cold-finger (-78 °C) and into 100 mL cyclohexane under argon. t-BuLi (20 mL, 1.5 M in pentane) was added rapidly and the stirred mixture was warmed up to 40 °C until the reaction started. After the initial reaction the mixture was kept at 50 °C for 3 hrs. and then quenched with D₂O (5 mL). The organic phase was dried and evaporated to dryness. Yield: 28.3 g (75 %).

6) PEP-h (**Va**).

Pd/C 10 % (3 g) in 100 mL of cyclohexane and 32 g of (**IVa**) was hydrogenated with an initial hydrogen pressure of 4 Bar for 1 hr. The reaction mixture was filtered through MgSO₄ and evaporated to give a colorless oil. After drying for 3 days at 80°C/200mmHg the oil was characterized. Yield: 30.1 g (91 %).

7) PEP-d (**Vb**)

PEP-d was prepared from 28 g **IVb** by hydrogenation with D₂ using the procedure described for **Va**. Yield: 25.3g (86 %).

Results and Discussion

The viscosity of the oil used for X-ray studies were measured to be 0.09 Pa s. From this the required degree of polymerization of a fully deuterated PEP was estimated to be 10 - 20 monomer units long. A synthesis of this polymer was devised and carried out as outlined in scheme.

Isoprene-d₈ has been prepared earlier via the Favorskii-Bergmann synthesis (1) where acetylene was first deprotonated with KOD in diglyme to a mixture of mono and di potassium acetylide. Reaction with deuterio-acetone afforded a mixture of 2-methyl-butynol and unwanted 2,4-dimethyl-butyn-2,4-diol which had to be separated and reduced the yield. In the present method the formation of the acetylide dianion is largely suppressed by using n-BuLi as a base at low temperature (-70 °C) (2). Further the distillation of the product in the original procedure was complicated by the azeotrope formed with D₂O upon distillation. In the present procedure no azeotrope was formed due to complete precipitation of the LiOD.D₂O thereby alleviating salts and D₂O. Reduction of (**I**) was carried out at high D₂ pressure over a Lindlar catalyst (Lead poisoned Pd/BaCO₃). The 2-methyl-butenol-d₁₀ (**II**) was dehydrated by vapor phase pyrolysis over neutral alumina at 300 °C. This was affected by slow evaporation of the alcohol in a stream of argon into a cylindrical oven packed with Al₂O₃ and condensing the products on to a cold finger. The oven temperature was found to be rather critical for the yield of isoprene. The isotopic purity of the crude isoprene-d₈ (**III**) was ascertained by 2H-NMR and GC-MS. Anionic polymerization was carried out by first distilling the

isoprene- d_8 from Al_2O_3 to remove any water, dissolving it in HPLC-grade cyclohexane and using $t-BuLi$ as initiator. In a last step the remaining double bonds in the PI-d were deuterated with D_2 over Pd/C in cyclohexane. The polymerisation and subsequent hydrogenation was first tested on isoprene- h_8 to ascertain that a polymer with the correct chain length and viscosity could be obtained. The polymers were characterized by SEC, NMR, MALDI-TOF MS, viscosimetry. The T_g was determined by DSC.

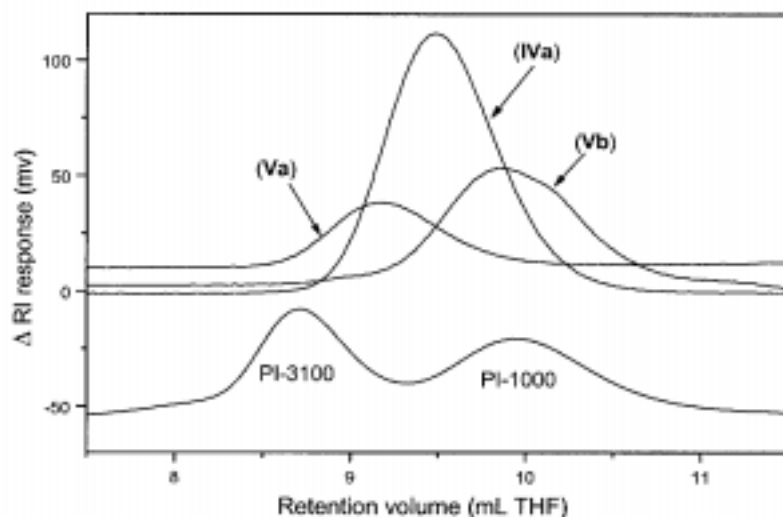


Figure 1. SEC of polymers **IVa**, **Va** and **Vb** with PI standards offset by -60 mV. The increase in apparent molar mass of from **IVa** to **Va** is due to an increase in the hydrodynamic volume.

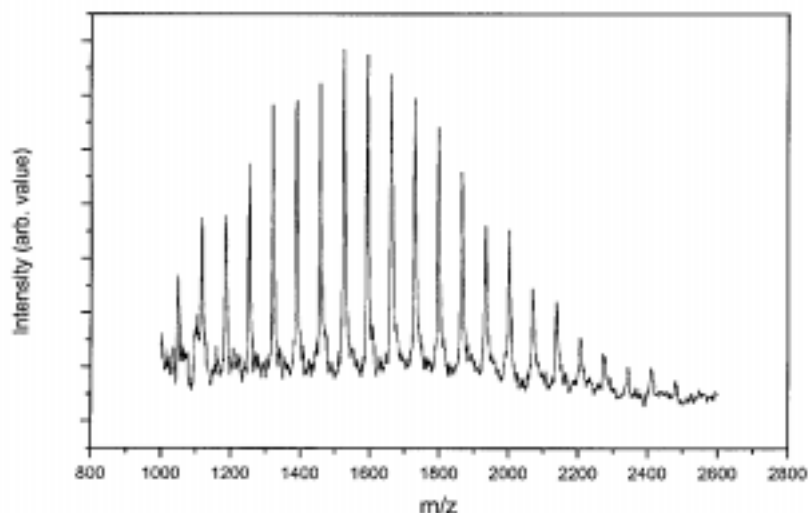


Figure 2. MALDI-TOF mass spectroscopy of polymer (**IVa**) using a dithranol matrix with $Ag^+ CF_3COO^-$. All peaks corresponds to an oligomer + Ag^+ with a mass difference of 68 consistent with the isoprene monomer.

Figure 1 shows the SEC data for the hydrogen and deuterium polymers (**IVa**), (**Va**) and (**Vb**) together with the standards polyisoprene 3200 and polyisoprene 1000. The SEC data were complemented by MALDI-TOF mass spectroscopy of (**IVa**) shown in figure 2. The molar mass determinations and polydispersity indices found are consistent and in the range expected. The fully hydrogenated or deuterated polymers could not be analyzed by MALDI-TOF MS, because the saturated systems are very hard to ionize with neither protons nor metal salts. Viscosity measurements at ambient temperature shows that the deuterated oil (**Vb**) has a somewhat higher viscosity than the standard X-ray oil. However, it is not so high that fast mixing with a crystalline material is hindered. All these data together with the glass transition temperature measured by DSC are collected in Table 1.

Table 1.
Data for the synthesised polymers **IVa**, **Va** and **Vb**.

	IVa	Va	Vb
Mw (g/mol)	1760 (1741)	1990	1.090
Mw/Mn	1.09 (1.06)	1.09	1.14
Tg (°C)	-78.5	-75.6	-69.9
η (Pa*s)	0.32	1.12	0.62

Numbers in parenthesis refers to MALDI-TOF data. Molecular masses determined by SEC were obtained by means of a PI calibration curve.

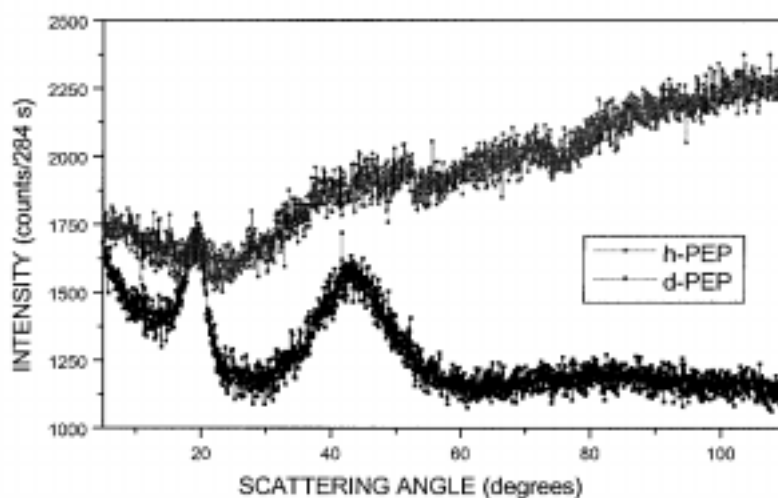


Figure 3. Neutron scattering data for the hydrogenated or deuterated PEP oils **Va** and **Vb**. (Incident neutron wavelength 1.56 Å).

Neutron diffraction experiments on both the hydrogenated and deuterated PEP oils (**Va** and **Vb**) were carried out at the TAS3 facility at the DR3 reactor at Risø National Laboratory to investigate the scattering characteristics at low temperature (8 K). Figure 3 shows the angle dependence of the neutron scattering efficiency of the two oils. It is clearly seen that the scattering efficiency is significantly smaller at higher angles for the deuterated oil. This is a desirable property since neutron scattering of the oil will attenuate signals from any crystalline sample that the oil has to protect. Two scattering

features can be observed at small angles corresponding to characteristic lengths of 2.1 and 4.7 Å. The first is a combination of CC bonds and CC nearest neighbors while the second is thought to arise from inter chain distances. Similar peaks could be expected for the h-PEP oil, but cannot be observed due to the isotropic scattering from hydrogen giving rise to a higher background. This illustrates the importance of deuterium substitution for neutron studies.

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