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Polymer 40 (1999) 4961–4964

polymer

Polymer Communication

Characterization of poly(2-propenoyl chloride) by nuclear magnetic resonance spectroscopy

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Received 20 July 1998; received in revised form 18 December 1998; accepted 18 December 1998

Abstract

A device to obtain the nuclear magnetic resonance (NMR) spectra of poly(2-propenoyl chloride) (PPC) avoiding any contact with the room moisture is described. The ^{1}H and ^{13}C NMR spectra of PPC in THF-d_8 solution are thus obtained. The distribution of meso and racemic dyads inferred from the integration of different ^{1}H NMR signals is: (m) = 0.45 and (r) = 0.55. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Anhydrous radical polymerization; 2-propenoyl chloride [814-68-6]; Poly(2-propenoyl chloride) [25 189-84-8]

1. Introduction

Poly(2-propenoyl chloride) (PPC) [25 189-84-8] is easily obtained by the free radical polymerization of 2-propenoyl chloride [814-68-6] [1–7]. Its copolymerization is also easily achieved by common monomers such as methyl methacrylate [8], acrylonitrile [9] or styrene [10].

PPC is interesting because of its capacity to react with alcohol- or amine-group compounds to yield polymers containing ester or amide groups. Thus PPC has been the subject of approximately 250 publications and patents since 1955 [7].

Although nuclear magnetic resonance (NMR) spectroscopy is the preferred method for polymer characterization, no NMR spectra of PPC had been published before. This can be explained by the fact that it is difficult to measure any NMR spectrum without partially hydrolyzing the polymer on air contact or by any residual water-content in the solvents used it was shown, ([11]) ''[…] the results of the hydrolysis of poly(acryloyl chloride) at 20°C at a water content of 2.78 mol/l. As is seen, the reaction is also of a pseudo-first order, and the rate constant was found to be $8.1 \times 10^{-3}\,s^{-1}$, so many several thousand times higher than for poly(methacryloyl chloride'').

In this article a method that allows the preparation and measurement of ^{1}H and ^{13}C NMR spectra of PPC avoiding any contact with room moisture is described.

2. Experimental

2.1. Preparation of poly(2-propenoyl chloride)

2-Propenoyl chloride (Aldrich) is distilled between 74 and 75°C on copper strips, under nitrogen atmosphere and is stored in a dry place. Fig. 1 shows a schematic setup of the apparatus used to polymerize 2-propenoyl chloride, to solubilize PPC in an anhydrous solvent and to transfer the solution to an NMR tube in rigorous dry conditions.

Recrystallized azobisisobutyronitrile (5.2 mg, AIBN—Aldrich product) is placed into an NMR tube 5 mm in diameter (part C in Fig. 1). A vacuum (0.1 mmHg) is established by opening all the Rotaflo tops and the device is swept by the flame of a Bunsen burner. 3 ml of 2-propenoyl chloride is introduced through a septum in part A of the device. As Rotaflo's 1and 3 are screwed on and part B is immersed into liquid nitrogen, a static vacuum is established and 2-propenoyl chloride is distilled from part A to part B. Similarly, 2-propenoyl chloride is once again distilled from part B to part C, to get a volume of around 0.5 ml. After three cycles nitrogen/vacuum, the apparatus is kept under nitrogen atmosphere by screwing on the Rotaflo's. Part C is immersed into a thermoregulated bath at 55°C for 105 min.

The vacuum is restablished later to eliminate the nonpolymerized 2-propenoyl chloride. Approximately 75 mg of $LiAlH_4$ is introduced through inlet D (no septum) which is retained in part A. The septum is replaced, and on keeping Rotaflo's 1 and 3 screwed on, part A is once again dried up as in the previous experiment. Tetrahydrofuran-d_8 (1 ml, TDE—Aldrich) is added through the septum. After a 2 h

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PII: S0032-3861(98)00868-4

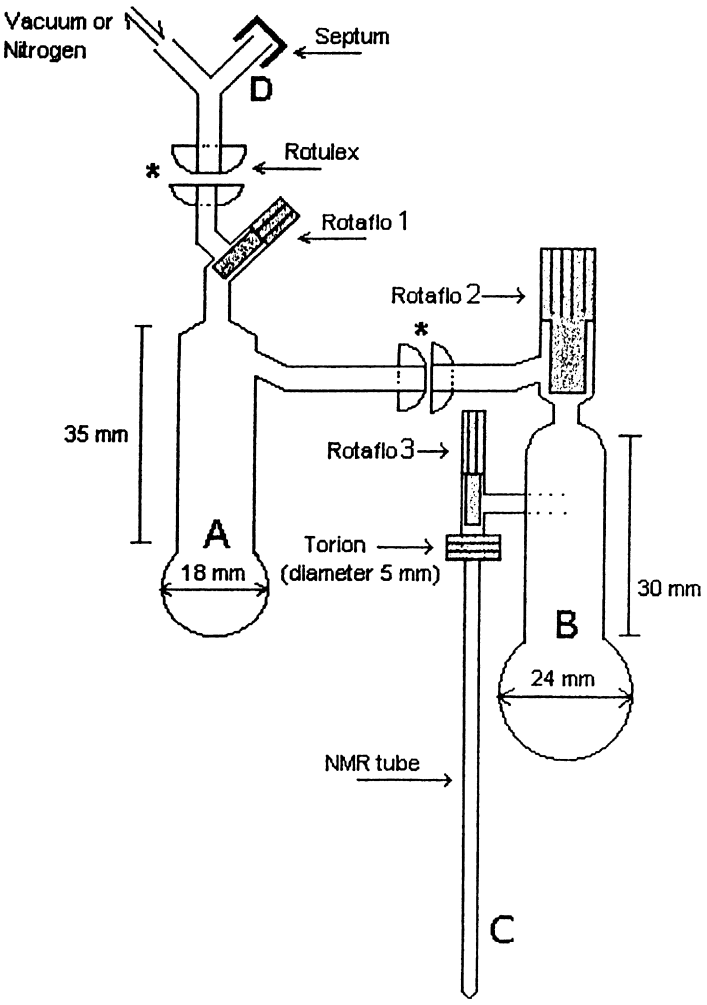


Fig. 1. Experimental device for the polymerization of 2-propenoyl chloride, the dissolution of PPC in TDF solution and filling an NMR tube in anhydrous conditions (* ground attachment clips are not represented).

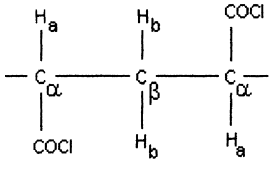
contact with $LiAlH_4$, TDF is distilled from part A through tube C, which is sealed off under vacuum, once its content was frozen with liquid nitrogen. This tube is used to measure the NMR spectra.

2.2. NMR measurements

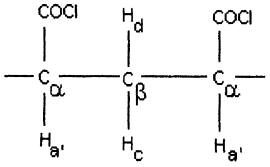
The chemical shifts are referred to normal THF with signals at 1.728 and 3.581 ppm for NMR ^1H spectra and at 25.328 and 67.413 ppm for NMR ^{13}C spectra. NMR spectra were measured at 295 K using a Bruker AMX-400 spectrometer operating at 400.13 MHz with a total of 64 scans for ^1H NMR and at 100.62 MHz for ^{13}C NMR with a total of 2048 scans.

3. Results and discussion

Fig. 2 shows the ^1H NMR spectrum of a solution of PPC in TDF.



Racemic dyad r



Meso dyad m

In the first approach, it can be considered that the tactic sequences consist of a mixture of meso (m) and racemic (r) dyads such as:

$$(m) + (r) = 1.$$

For a perfectly syndiotactic sequence of infinite length, the methylene protons H_b are identical and give a singlet signal split by the presence of H_a. For a perfectly isotactic sequence of infinite length, the non-equivalent methylene

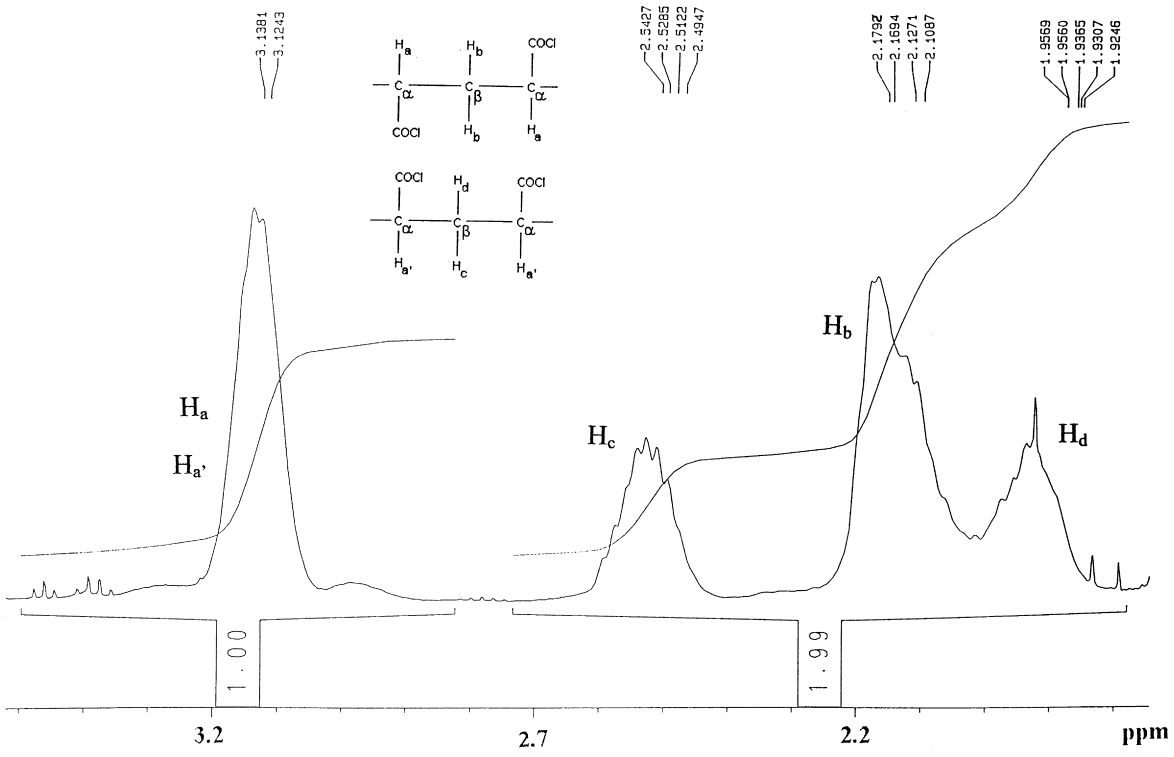


Fig. 2. The 400 MHz ^{1}H NMR spectrum of a solution of PPC in TDF, temperature 295 K.

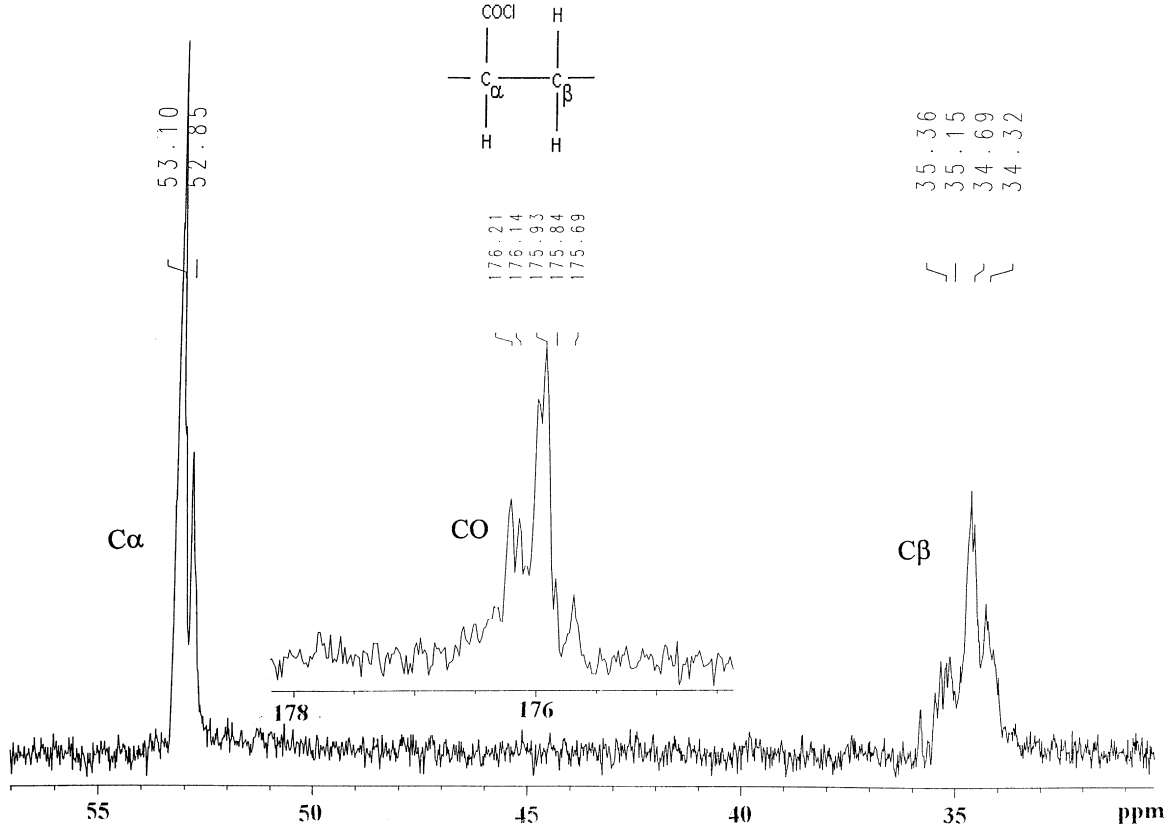


Fig. 3. The 100 MHz ^{13}C NMR spectrum of a solution of PPC in TDF, temperature 295 K.

protons H_c and H_d give a split doublet because of the presence of $H_{a'}$.

Experimentally, according to the different tactic sequences surrounding the meso dyads, the chemical shifts will bring about the juxtaposition of the split doublets resulting in two broad signals between 1.85 and 2.05 ppm for H_d and between 2.45 and 2.60 ppm for H_c. The same is true of the racemic dyads, giving a broad signal between 2.06 and 2.25 ppm for H_b. The distribution of the dyads (m) and (r) are obtained from their respective intensities:

$$(m) = 0.45 \quad \text{and} \quad (r) = 0.55.$$

The band between 3.05 and 3.20 ppm corresponds to H_a and $H_{a'}$ protons, which are situated at the carbonyl's α position.

The three series of peaks between 5 and 6 ppm correspond to the protons of residual 2-propenoyl chloride which represents 0.9% of the PPC content. A low intensity resonance band is observed at 8.65 ppm. From this band, which is attributable to the carboxylic acid protons, it is inferred that there is only 0.18% poly(acrylic acid). The peak found at 1.672 ppm corresponds to AIBN's methyl groups.

The ^{13}C NMR spectrum of PPC in TDF solution is shown in Fig. 3. In the carbonyl region, a series of fine peaks can be seen between 175.60 and 176.30 ppm. Also, in the methylene and methyne carbon regions there are two groups of peaks situated between 34.10 and 35.50 ppm and between 52.50 and 53.30 ppm which correspond, respectively, to the methylene carbons (C_β) and to the methyne carbons (C_α). The multiplicity of the peaks reflect the existence of different configurations of the polymer chain.

4. Conclusion

The polymerization of 2-propenoyl chloride in an anhydrous and closed system has made it possible to obtain PPC with more than 99.8% of non-hydrolyzed components. NMR ^1H and ^{13}C spectra are presented and analyzed here.

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