

Anionic synthesis and thermal properties of poly(3,3-diethylthietane)

Silvia Lazcano*, Antonio Bello, Carlos Marco, and José G. Fatou

Instituto de Ciencia y Tecnología de Polímeros, Juan de la Cierva, 3, E-28006 Madrid, Spain

Summary

3,3-Diethylthietane has been polymerized by means of the anionic initiators butyl lithium and naphthalene sodium. Linear poly(3,3-diethylthietane) samples have been obtained. The molecular weight of these polymers, measured by GPC, ranges from 70,000 to 241,000. The molecular weight distribution is quite narrow. Calorimetric measurements show a glass transition temperature, extrapolated to zero heating rate, of 236.7 K. The melting curves of a sample isothermally crystallized from the melt at 303 K show two different melting peaks located at 326 and 334 K, respectively. The wide angle X-ray diffractograms for poly(3,3-diethylthietane) crystallized at 303 and 330 K gave identical patterns. Microscopy and small angle light scattering observations show that the supermolecular structure corresponds to ordered spherulites.

Introduction

Polythietanes, of general structure $[-S-CH_2-CR_1R_2-CH_2-]_n$, form a type of polysulfide whose properties may differ depending on the method of preparation. They can be prepared by means of ionic polymerization and the synthesis of polythietanes using cationic initiators such as triethylaluminium, phosphorus pentafluoride and trimethyloxonium tetrafluoroborate has been reported (1-4). Initiation consists on monomer alkylation and a cyclic sulfonium ion is formed, which is the active species in the propagating step. Nevertheless, a termination reaction occurs if instead of the monomer, a sulfur atom of an already formed polymer reacts with the cyclic sulfonium ion. This reaction leads to a non-strained sulfonium ion which cannot re-initiate the polymerization. This is reflected by the formation of polymers with branched structures (4).

However, linear polythietanes can be prepared by using anionic initiators such as butyl lithium and naphthalene sodium (5,6). Previous results of this laboratory have been concerned with the anionic synthesis of three members of this series, polythietane (7), poly(3,3-dimethylthietane) and poly(3-ethyl-3-methylthietane) (8), in order to obtain polymers of structural regularity. Dilute solution properties, thermal transitions and crystallization behaviour of these polysulfides have been analyzed (9-12).

Since substituents considerably modify the physical properties of polythietanes, the aim of this work is to obtain regular poly(3,3-diethylthietane), PDET, and to describe some thermal properties of this polymer.

*To whom offprint requests should be sent

Experimental

a) Synthesis:

The monomer, 3,3-diethylthietane, was prepared by means of two consecutive reactions, using the method of Searles (13). The crude reaction product was distilled at nitrogen atmosphere and stirred over CaH_2 for 12h. After that, it was distilled in a vacuum line several times from sodium mirror and then from butyl lithium, at temperatures below 0°C , and stirred until incipient polymerization.

The polymerization solvent, tetrahydrofuran, THF, was refluxed over KOH, distilled first in a vacuum line several times from sodium mirrors and then from potassium mirrors. Hexane and benzene were distilled under vacuum from butyl lithium.

The initiating agent, butyl lithium, was prepared from butyl chloride and metallic lithium in hexane. The initiator solution was filtered in vacuum, dried and redissolved. The concentration of the solution was evaluated by reaction with styrene and measurement in a spectrophotometer UV-V Cary-14. Naphthalene sodium was prepared from naphthalene and metallic sodium in THF. The increase of the initiator concentration with the reaction time was followed by UV spectroscopy.

Polymerizations were performed in THF at -78°C under high-vacuum conditions. Round flasks connected through stopcocks with various tubes containing the different products were used. Methanol was added before opening the apparatus to the atmosphere. Reaction mixtures were evaporated and, after drying, polymers were analyzed by GPC in a Waters 150_3C apparatus with microstyragel columns of nominal sizes 10^6 , 10^5 , 10^4 , 10^3 , 5×10^2 , and 10^2 Å calibrated with polystyrene standards.

b) Characterization:

The $^1\text{H-NMR}$ spectrum was determined at 100 MHz in CDCl_3 with tetramethylsilane as internal reference. The spectrum showed three absorptions: a single peak at 2,57 ppm and two multiplets at 1,43 and 0,82 ppm, corresponding to methyl and methylene groups of the lateral chains and methylene groups of the main chain, respectively.

Intrinsic viscosity measurements were determined using an Ubbelohde viscometer in THF solutions at 25°C .

A Mettler TA-3000 with a DSC-30 head was used for obtaining transition temperatures and heat capacities. Samples were molten for 10 min at 373 K. Microscopy studies were carried out using a Reichert polarizing microscope, Zetopan Pol. Small angle light scattering (SALS) studies were carried out with equipment similar to that described by Stein (14).

X-ray diffractograms were obtained with a Geiger counter X-ray diffractometer made by Phillips Co. The diffractograms were recorded in the 2θ range between 4° and 35° , using a Ni-filtered $\text{CuK}\alpha$ radiation.

Results and Discussion

Butyl lithium and naphthalene sodium have been used to polymerize 3,3-diethylthietane in THF at -78°C , leading to the results summarized in Table I for various C/I ratios, C and I being the initial molar concentrations of monomer and initiator, respectively.

These initiator systems were used in previous works to polymerize thietane (5-7), 3,3-dimethylthietane and 3-ethyl, 3-methylthietane (8). In the first case, some termination reaction occurs and polymers of low molecular weights and with low yields are obtained, although it is possible to increase the conversion in non polar solvents, increasing the size of the "contraion" and, in polar solvents, increasing the polarity of the medium (7). However, when 3,3-dimethyl and 3-ethyl, 3-methylthietane are polymerized using these initiating systems, quantitative yields of polymer

TABLE I
Data for 3,3-diethylthietane polymerization

| Exp | Initiator | $(C_o/I_o) \times 10^{-2}$ | Conv (%) | M_p^{GPC} | $[\eta]_{THF, 25^\circ C}$ | Mw/Mn |
|-----|-----------|----------------------------|----------|-------------|----------------------------|-------|
| 1 | Bu Li | 8.5 | 46 | 59,900 | 0.25 | 1.36 |
| 2 | Bu Li | 9.8 | 52 | 82,700 | 0.32 | 1.27 |
| 3 | Naph Na | 6.6 | 68 | 178,100 | 0.72 | 1.71 |

of narrow molecular weight distribution are obtained. For 3,3-diethyl thietane, several hours are needed to reach the conversion quoted in table I. Yields were not quantitative. On the contrary, the polymerizations for 2-methylthietane (5), 3,3-dimethylthietane and 3-ethyl-3-methylthietane (8), at the same conditions, gave quantitative yields. As it has been shown (8), there is no termination process in the polymerization of other 3,3-disubstituted thietanes using these anionic initiators. Several facts, like the existence of a low ceiling temperature may be responsible of such reduced yields for 3,3-diethylthietane polymerizations at $-78^\circ C$ and they will be investigated subsequently.

Nevertheless, the obtained samples have quite narrow molecular weight distribution, specially if butyl lithium has been used as initiator. The same effect has been found for the other polythietanes and it has been explained by a faster initiation step in the butyl lithium polymerization (8).

In this work linear PDET samples have been obtained. The molecular weight of the obtained polymers has been measured by means of GPC and ranges from 70,000 to 241,000 with Mw/Mn ratio from 1.27 to 1.71 (Table I).

Calorimetric measurements were carried out on the sample of molecular weight 93,000 to determine thermal transitions of PDET. The polymer quenched at 123 K from the molten state and heated at 1-10 K/min shows a significant change in heat capacity between 237 and 243 K, depending on the heating rate. In these conditions, the polymer is obtained in a totally amorphous state, as confirmed by the absence of any endotherm or exotherm peak on the DSC traces, and the observed change in heat capacity corresponds to the glass transition. In order to eliminate the influence of the heating rate, T_g was determined by extrapolating to zero heating rate (Fig. 1). The extrapolated value was of 236,7 K and the corresponding change in the heat capacity, $\Delta C_p(T_g)$, was of $45.6 \text{ J mol}^{-1} \text{ K}^{-1}$ at 1 K/min.

PDET does not crystallize, neither on heating from the glassy state at 1-10 K/min nor on cooling from the melt at the same rates, probably due to kinetic factors. However, when isothermal annealing is used PDET crystallizes, showing a definite WAXS diagram, Fig. 2, with maximums at $2\theta = 8.5, 15.7, 16.9$ and 18.3° .

The morphology observed for PDET in the analyzed crystallization temperature range corresponds to spherulites of very little sizes. The small angle light scattering, SALS, analysis showed typical four-fold clover appearances with symmetric Hv scattering patterns, corresponding to ordered spherulites.

Fig. 3 shows the melting curves for PDET isothermally crystallized from the melt at 303 K for 18 h obtained at a heating rate of 5 K/min. Both

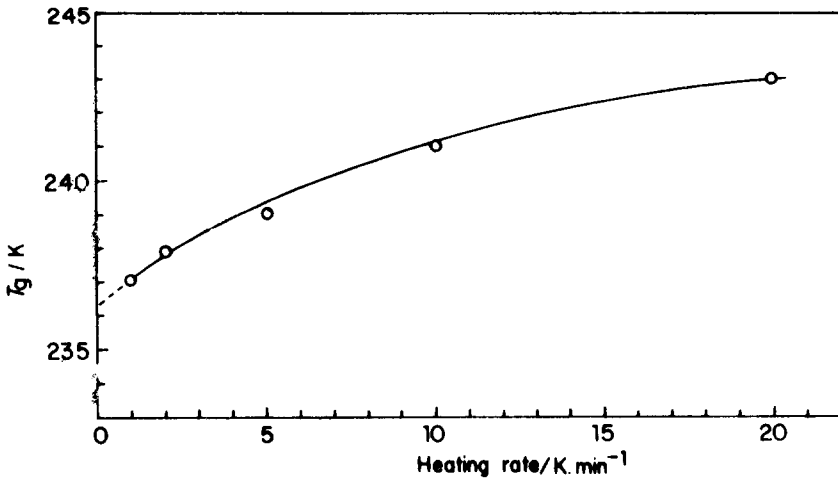


Figure 1.- Glass transition temperature of quenched PDET as a function of heating rate

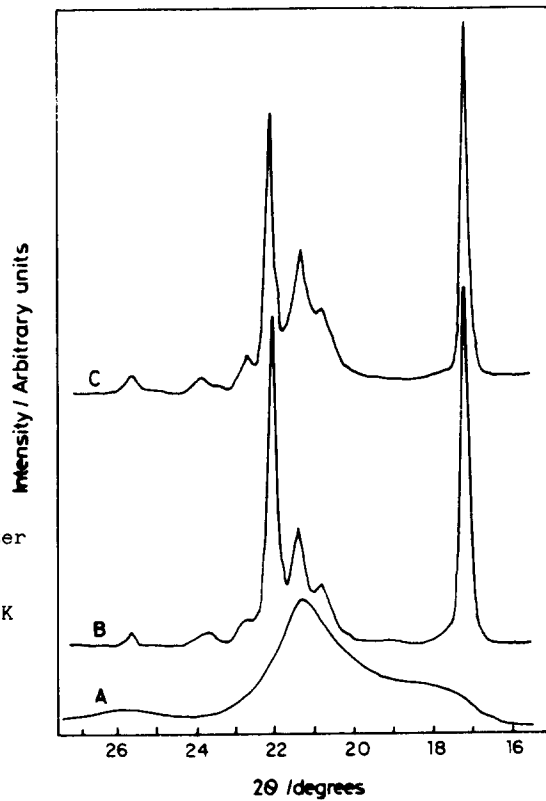


Figure 2.- X-ray diffractometer scans of amorphous PDET (A) and PDET crystallized at 303 K (B) and 330 K (C)

curves show two different melting peaks. The sample crystallized for 18 h shows the low-temperature peak at 326 K and the high-temperature peak at 334 K.

Multiple melting peaks have been described in other polymeric systems (15) and assigned to different crystalline fractions differing in size, perfection and/or crystalline order. Fig. 2 shows the X-ray diffractograms obtained at two different crystallization temperatures, of 303 and 330 K, respectively. The diffractograms are identical each other, excluding the polymorphism in our samples. Moreover, the GPC analysis of the PDET sample showed the molecular weight distribution to be quite narrow, excluding the possibility of different molecular weight chains contributing to the presence of two melting peaks. Thus, the melting behaviour of PDET may be due to a reorganization process in the dynamic experiment. Nevertheless, experiments in order to study this effect are in course and they will be described in a further paper (16).

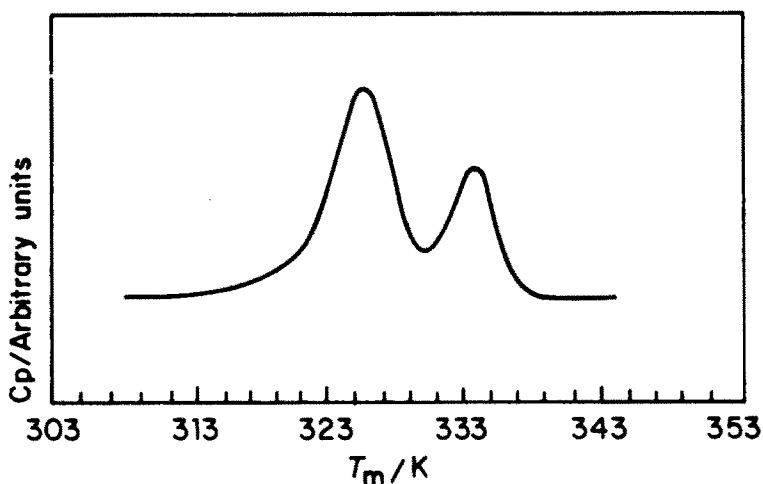


Figure 3.— DSC fusion trace at a heating rate of 5 K/min of PDET crystallized at 303 K for 1200 min

Acknowledgement

We acknowledge financial support of the Comisión Asesora de Investigación Científica y Técnica, CAICYT, to the Project n^o 568.

References

1. Foldi VS, Sweeney W (1964) Makromol Chem 72: 208
2. Stille JK, Empen JA (1967) J Polym Sci A1 5 : 171
3. Price, CC, Blair EA (1967) J Polym Sci A1 5: 171
4. Goethals EJ, Drijvers W, Van Ooteghen D, Buyle AM (1973) J Macromol Sci Chem 7: 1375
5. Morton M, Kammerreck RF, Fetters LJ (1971) Br Polym J 3: 120
6. Paulet R, Etienne Y (1967) Ind Chim Belge 32 esp: 385

7. Sánchez A, Bello A, Marco C, Fatou JG, to be published
8. Lazcano S, Bello A, Marco C, Fatou JG, to be published
9. Sánchez A, Bello A, Marco C, Fatou JG (1988) Makromol Chem 198: 399
10. Sánchez A, Marco C, Fatou JG, Bello A (1988) Eur Polym J 24: 355
11. Lazcano S, Bello A, Marco C, Fatou JG (1988) Eur Polym J 24: 985
12. Lazcano S, Marco C, Fatou JG, Bello A (1988) Eur Polym J 24: 991
13. Searles S, Hayes HR, Lutz EF (1962) J Org Chem 27: 2828
14. Stein RS (1964) New methods of polymer characterization, Ke B (ed), Wiley-Interscience, New York
15. Mandelkern L, Fatou JG, Denison R, Justin J (1965) J Polym Sci B3:803
16. Marco C, Lazcano S, Fatou JG, to be published

Accepted April 1, 1989 C