Sulfonation of nylon-6 by solid phase reaction

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Sulfonation of nylon-6 has been widely studied via solution phase reaction processes, which involve dissolution of the base polymer in a strong solvent. In this paper, novel solid phase reaction technology was adopted to induce the addition of the sulfonate side chain onto the backbone of nylon-6 using 1,3-propane sultone. The reaction of the polymer with the reagent, which was catalysed by dimsyl anions, was carried out at 65°C in a specially designed, well-mixed reactor. The reaction materials remained as free-flowing powders through the process. A sulfonate level of 1.32 mol% was achieved. The conversion of the 1,3-propane sultone was 23.3%. The sulfonation was qualitatively identified with *FT*i.r. and d.s.c. Its sulfonate level was determined by quantitative measurement of sulfur and nitrogen content of the treated polymer.

(Keywords: solid phase reaction; sulfonation; nylon-6)

Introduction

The combination of low ionic content and non-polar backbone results in a class of commercial polymers which is referred to as 'ionomers'. Unlike homogeneous polymer systems, pendent ionic groups (carboxylate, sulfonate or phosphonate) interact to form ion-rich aggregates contained in the polymer matrix[1]. The resulting ionic interactions strongly influence polymer properties and applications.

Sulfonated polymers, in particular, exhibit extremely strong ionic interactions, even at low ionic concentrations, owing to the high degrees of polarity inherent in such systems[2]. For example, the modification of nylon-6 with sulfonate groups improves permeation[3] and dye retention properties. Sulfonated nylon-6 also has potential applicability as an ionomer compatibilizer[4,5] in polymer blends.

This paper is focused on the sulfonation of nylon-6 with 1,3-propane sultone using the solid phase reaction process[6–8]. The technology of solid phase reaction, which is a low temperature and low pressure process, uses only a small amount of solvent as an interfacial agent, and no, or minimal, solvent recovery is necessary. However, the reaction yield in solid phase processes is somewhat low compared to that of conventional solution phase processes because of low diffusivity of the comonomer in the solid phase and the inaccessibility of the crystalline regions in the base polymer. This must be weighed against using conventional solution phase reactions for polymer modification because such reactions require the use of excessive amounts of environmentally hazardous solvents to dissolve the polymer. The conventional solution phase process is efficient in terms of the high level of conversion achieved, but is very expensive and uneconomical owing to the high cost involved in solvent separation and pollution problems.

Experimental

Materials. Nylon-6 was obtained from Allied Signal Inc. in the form of pellets. It was ground cryogenically into a powder (− 30 + 40 US mesh) to increase the surface area. The sample was dried in a vacuum oven just prior to use. 1,3-Propane sultone and dimethyl sulfoxide (DMSO) were obtained from Aldrich Chemical Co. and were used as received. Since the sodium hydride reacts explosively with moisture in the atmosphere, 60% sodium hydride dispersed in mineral oil was obtained from Aldrich Chemical Co. and used as received.

Equipment. A stainless steel reactor (800 ml), equipped with specially designed blades for effective polymer powder mixing, was used for the solid phase reaction. Flexible heating tape around the reactor ensured a uniform temperature inside the reactor. A thermocouple was installed to measure the reaction temperature by direct contact with the reaction ingredients. Nitrogen was used to maintain an inert atmosphere inside the reactor prior to the addition of reagents. A sampling valve was mounted at the side of the reactor, which facilitated sampling of the reaction materials for observation of reaction kinetics. A vacuum line was connected to the sampling valve for convenient extraction of samples from the reactor.

Since DMSO and dimsyl anion ($CH_3SOCH_2^-$) are exceedingly moisture-sensitive reagents, extreme care was taken to prevent exposure to the atmosphere. The syringe transfer or double-tipped needle transfer method for handling air-sensitive reagents was adopted for transferring measured amounts of reagents.

Reaction procedure. The mixing of sodium hydride (0.05 mol) in dry DMSO (0.256 mol) at 70°C for 1 h with nitrogen purging generated the powerfully basic dimsyl anion. All operations involving sodium hydride and DMSO were conducted in a glove box with an inert atmosphere of dry nitrogen. The dimsyl solution

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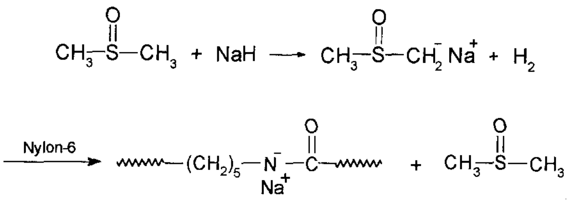
was added to the nylon-6 powder (0.884 mol amide unit = 100 g) for amide anion formation. The mixture was reacted at 65°C for 30 min under dry nitrogen. After the metalation reaction, 0.05 mol of 1,3-propane sultone was added to the reaction mixture at 65°C. The reaction was continued for 1 h with effective mixing and nitrogen purging.

Purification and characterization. In order to remove all traces of unreacted 1,3-propane sultone and DMSO, the product was extracted continuously in a Soxhlet extractor for at least 48 h using petroleum ether as the solvent[9]. Drying in a vacuum oven at 100°C was required to remove the physically bound DMSO. To confirm complete removal of residual DMSO, which is very difficult to remove because of its polarity and high boiling point, dimsyl solution was mixed with nylon-6 powder at the metalation reaction conditions mentioned previously, and extracted by the aforementioned purification procedure. The extracted sample was characterized by *FT*i.r. and a homopolymer nylon-6 free of DMSO was obtained. The product was characterized with *FT*i.r. (Bio-Rad FTS7) using a thin film cast from a solution obtained with *m*-cresol.

The instrument used for d.s.c. was a DuPont model 910 differential thermal analyser. The sample was dried before analysis in a vacuum oven at 80°C for 8 h. All runs were made in a dry nitrogen atmosphere. Each sample was heated to 260°C followed by immediate quenching in liquid nitrogen, and then analysed at 10°C min^{-1}. To determine the sulfonate level, C, H, N and S elemental analyses were carried out using a LECO-CHN 600 CHN-determinator and a LECO-SC132 sulfur determinator.

Results and discussion

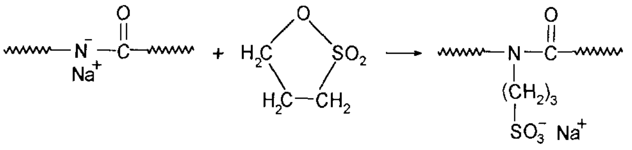
Polymer modification. DMSO reacted with sodium hydride to form a dimsyl anion solution. It was also used as a swelling and interfacial agent owing to its high polarity. A small amount of appropriate solvent (10–20 wt%) increases the reaction surface area by swelling the polymer, thus increasing the conversion level[7]. The reaction pathway[10–13] may be represented by:



$$CH_3-\overset{O}{\overset{\parallel}{S}}-CH_3 + NaH \longrightarrow CH_3-\overset{O}{\overset{\parallel}{S}}-\overset{-}{C}H_2\,\overset{+}{Na} + H_2$$

$$\xrightarrow{\text{Nylon-6}} \sim\sim(CH_2)_5-\underset{Na^+}{\overset{-}{N}}-\overset{O}{\overset{\parallel}{C}}-\sim\sim + CH_3-\overset{O}{\overset{\parallel}{S}}-CH_3$$

The unshared electron pair of metalated nylon-6, a very strong base, attacks 1,3-propane sultone by the S_N2 mechanism, which results in ring-opening at the carbon–oxygen bond[13].



*FT*i.r. *analysis.* The qualitative confirmation of alkylsulfonation was obtained from the *FT*i.r. spectra. The strong absorption due to sulfur–oxygen double bonds (S=O) characteristic of sulfonic acid salts appears at 1150–1250 cm^{-1} for asymmetric stretching and at 1040–1070 cm^{-1} for symmetric stretching[14,15]. The peaks are clearly seen by comparison of a spectrum of nylon-6 homopolymer with that of sulfonated nylon-6, as shown in *Figure 1*. This confirms the successful addition of the sulfonate group onto the solid nylon-6.

Thermal analysis. One of the major changes of physical properties caused by the introduction of ionic

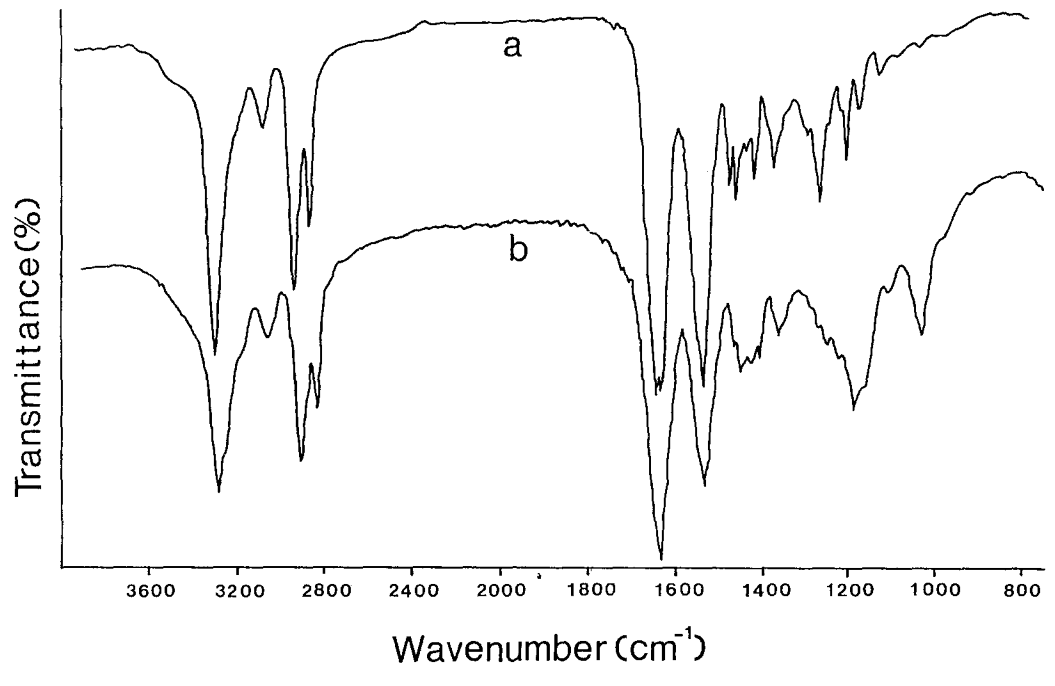


Figure 1 *FT*i.r. spectra of (a) nylon-6 homopolymer and (b) sulfonated nylon-6

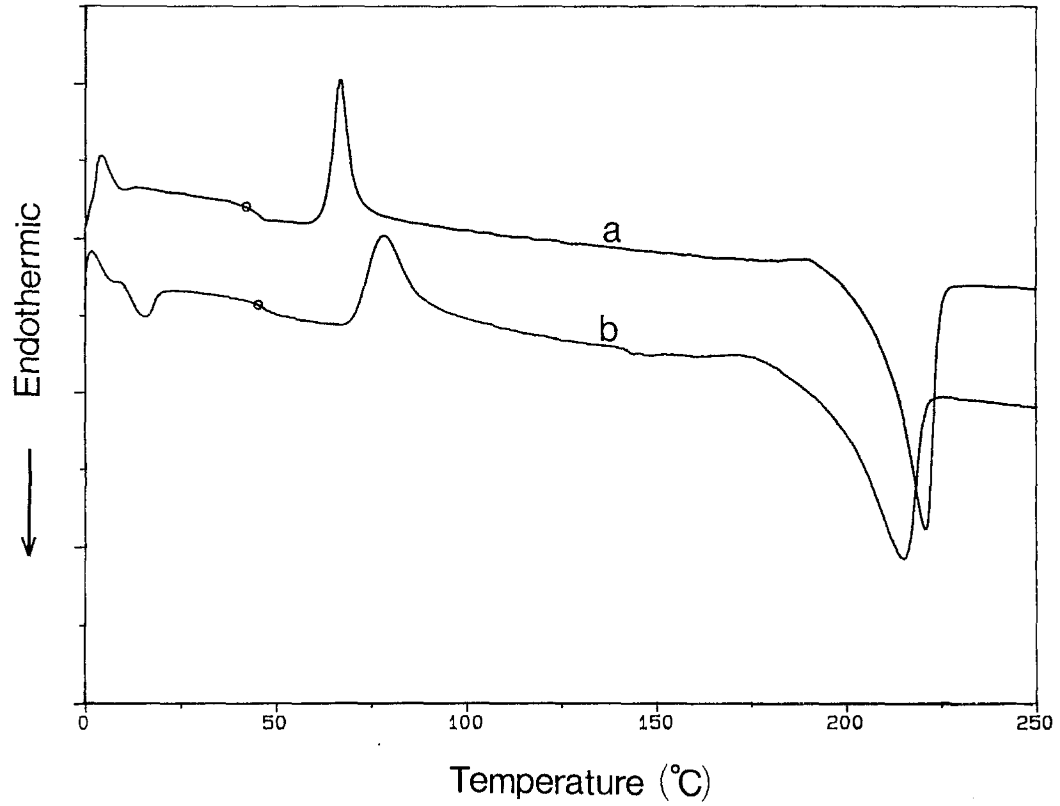


Figure 2 D.s.c. heating curves of (a) homopolymer nylon-6 and (b) sulfonated nylon-6, with glass transition points marked by circles

groups into polymer chains is an increase in the glass transition temperature (T_g), which results from physical crosslinks formed by ionic association and restricted mobility of the backbone. D.s.c. results for nylon-6 homopolymer and sulfonated nylon-6 are displayed in *Figure 2*. The T_g was defined by the onset of the transition, as marked by circles in *Figure 2*. The peak temperature of the melting endotherm was taken as the melting point of the polymer. The nylon-6 homopolymer exhibits a distinct T_g at 42°C, followed by an exotherm centred around 67°C and an endotherm that appears around 221°C. Sulfonated nylon-6 shows a slightly higher T_g (45°C) and broadened exotherm centred at 78°C. The melting endotherm is broader and shows a lower melting temperature centred at 214°C. The effects of sulfonate groups on morphology, such as changes in size and perfection of the crystallites, are responsible for the depression and broadening of the melting point. The increase of T_g and the depression of the melting point are expected, and are consistent with the successful addition of sulfonate groups onto nylon-6.

Elemental analysis for quantitative characterization. The weight percentages of sulfur and nitrogen contents were 0.35% and 11.56%, respectively, for the sulfonated sample. The mole percentage of sulfonate side chains was calculated by obtaining the mole ratio of nitrogen and sulfur in the sulfonated nylon-6 as follows:

$$\text{mol\% of sulfonate groups} = \frac{\text{wt\% of S}/32.06}{\text{wt\% of N}/14.0067}$$

The mole percentage of sulfonated groups in the product is thus 1.32%. This is equivalent to 23.3% conversion of the 1,3-propane sultone added onto the nylon-6 backbone chain.

Conclusions

A novel solid phase reaction technique was successfully employed to introduce 1,3-propane sultone onto nylon-6. The process possesses merits of low temperature and low solvent operation. The sulfonated polymer was characterized by *FT*i.r. and d.s.c. for qualitative identification of sulfonate side chains. Sulfur and nitrogen analyses gave a quantitative measure of the sulfonate level.

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