Preparation and Properties of Some Poly(alpha-olefin Sulfones)

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Synopsis

The properties of alpha-olefin–sulfur dioxide copolymer prepared from the series C_8–C_{18} (even-numbered) alpha-olefins and sulfur dioxide are described. These polymers undergo clean thermal degradation and have high permeabilities to oxygen and carbon dioxide. Maximum permeabilities, maximum per cent elongation at the yield point, and minimum density are obtained with the C_{16}-based polymer. An explanation is proposed involving a competitive plasticizing/side chain crystallization effect.

INTRODUCTION

Copolymers from simple olefins and SO_2 have been known for some time They were first reported by Matthews and Elder[1] in 1915, although the material prepared was not identified as being polymeric. Seyers and King[2] in 1933 were the first to accurately describe an olefin heteropolymer of sulfur dioxide. Characterization of these compounds as high molecular weight materials was accomplished independently by Marvel[3,4] and Staudinger.[5] Both recognized that an AB-type copolymer was obtained regardless of monomer concentration, and they correctly deduced that the active polymerizing species was an olefin–sulfur dioxide complex. Marvel and Weil[6] showed the polysulfone structure to be a head-to-tail configuration as evidenced from the preparation of various reference compounds that were compared with the hydrolysis products of the polymers.

Marvel[3,4,7] characterized a number of olefin–sulfur dioxide polymers using pyrolysis techniques. Naylor and Anderson[8] prepared copolymers of ethylene, propylene, 2-butene, and isobutylene with SO_2 at 65°–70°C using radical catalysts. They found that the propylene–sulfur dioxide polymer started to degrade at about 180°C with an activation energy of 32 kcal/mole determined from data obtained between 180° and 260°C (T_c for this polymer[9] is 62.5°C). Pyrolysis of the propylene-based polymer in nitrogen at 280°–290°C yielded 95.4% volatile products, with 83.4% of the initial polymer weight being monomers. Water and some unidentified sulfur-containing compounds were also isolated.

This paper describes the preparation and properties of poly(alpha-olefin sulfones) prepared from the series $C_8 \rightarrow C_{18}$ (even-numbered) alpha-olefins and sulfur dioxide.

EXPERIMENTAL

Monomer Purity

Commercial alpha-olefins having a minimum mono-olefin content of 98.5% (remainder being normal paraffins) were used in this study. Gas-chromatographic analysis showed less than 2% olefinic impurities consisting of other alpha-olefins.

Polymerization

Bulk polymerization was used to prepare the series based on the $C_6 \rightarrow C_{18}$ even-numbered alpha-olefins and sulfur dioxide. A clean, dry, nitrogen-purged citrate bottle was cooled in an ice-water bath, then liquified sulfur dioxide was added. The olefin containing 1% *tert*-butyl hydroperoxide, based on the olefin, was then added slowly to the citrate bottle. With an addition of a small amount of the olefin, approximately one fourth of the total quantity, a rapid reaction occurred, resulting in a loss of some SO_2. After the remaining olefin–peroxide mixture was added, the bottle was capped with a lined, ventable cap and the contents were allowed to warm to room temperature. Following a predetermined reaction period, usually 20 hr at room temperature, the bottle was vented and the contents were removed. The product was kept at reduced pressure to remove the residual monomers.

Molecular Weights

Molecular weights ($\bar{M}_n$) (membrane osmometer) were all above 100,000, and some were as high as 350,000.

Differential Thermal Analysis

Polymer melt temperatures were obtained using the standard capillary (micro) cell of the du Pont 900 instrument, the du Pont 900 with the DSC cell module, and visually using a Kofler melt bar. These data are shown in Figure 1. All melt data were obtained on polymers having molecular weights ($\bar{M}_n$) in excess of 150,000. It was not possible to obtain accurate glass transitions since several other second-order transformations appeared to be occurring in the temperature region where one would expect the T_g to occur.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was obtained on a du Pont 900 unit in both air and nitrogen atmospheres. For screening purposes for a particular polymerization run, a heating rate of 20°C/min in air with a sample size of about 10–15 mg was used. Generally the polymer decomposed cleanly. Pyrolysis started at 175°C and was essentially complete when the temperature reached 275°C. One C_{14} polymer sample ($\bar{M}_n$ 136,000) was used to obtain kinetic data (pyrolysis) using the method of Wall and
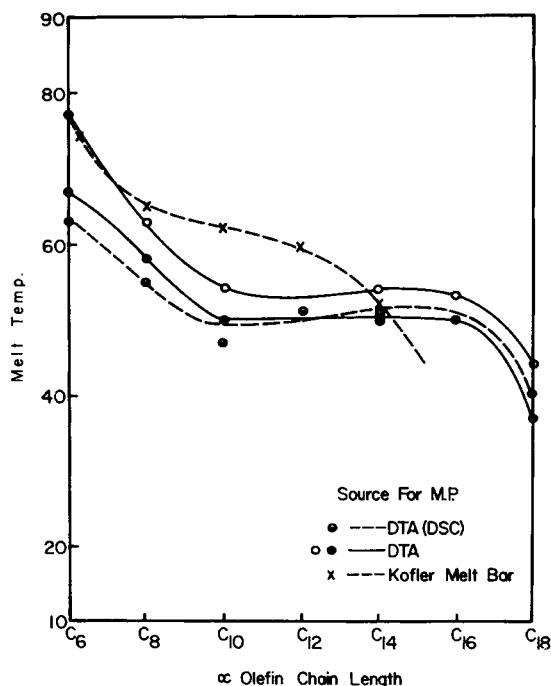
Fig. 1. Polymer melt temperatures vs. α-olefin chain length.

Flynn.[10]   TGA data were obtained at heating rates of 5, 10, 15, and 20°C/
min in air.   The average activation energy for the pyrolytic decomposition
was found to be 46–47 kcal/mole.

Mass-Spectrometric Thermal Analysis and Pyrolysis Gas-Chromatographic Analysis

Mass-spectrometric thermal analysis was accomplished using the solid
sample wand of the Varian M-66 mass spectrometer.   The sample used was
the C_{14} polymer used for the kinetic TGA runs.   A wand temperature of
250°C yielded mass spectra differing only from the fragmentation pattern of
the pure C_{14}-alpha-olefin by peaks at 64 and 48 mass units corresponding to
the SO_2 and SO ion species.

For higher-temperature pyrolysis studies, pyrolysis gas chromatography
was utilized.   A Perkin-Elmer pyrolyzer was connected to a gas chromato-
graph equipped with a hydrogen flame detector and a 20% carbowax/fire-
brik column.   Separate samples of the C_{14} copolymer were heated rapidly to
400°, 600°, and 800°C in the pyrolysis chamber.   At 400°C, only the C_{14}-
alpha-olefin was detected.   At 600°C, about equal amounts of the olefin
and lighter pyrolysis products were found, while at 800°C, only complete
pyrolysis products consisting of methane, ethylene, ethane, propylene, and
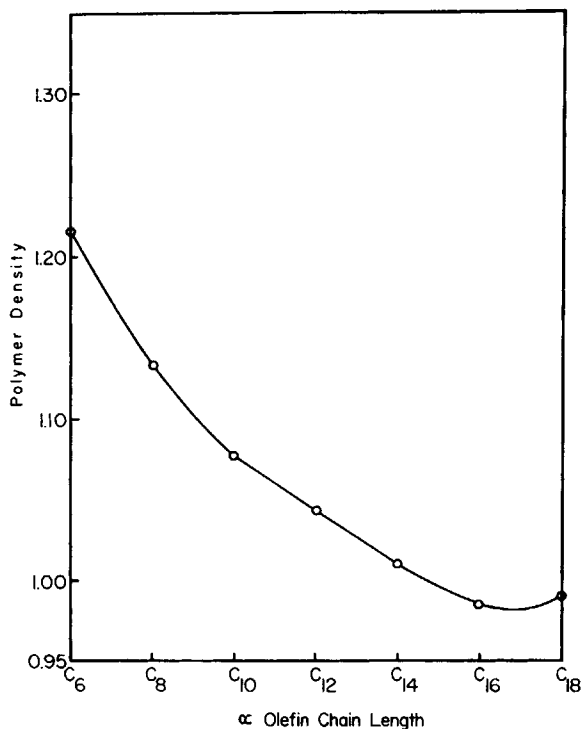propane were found.

Fig. 2. Density of the sulfone polymers vs. α-olefin chain length.

Density

Density as a function of chain length was determined on the polymer series using a density gradient column. These data are shown in Figure 2.

Permeability

The gaseous permeability to oxygen and carbon dioxide of this series of polymers is quite high, with only the silicones and modified silicones showing higher permeability. The relationship between alpha-olefin chain length and gaseous permeability (oxygen and carbon dioxide) for the C_8–C_{18} series is plotted in Figure 3. Permeability was determined by a modified Linde volumetric cell on films from polymers having molecular weights in excess of 150,000 ($\bar{M}_n$).

Tensile Modulus and Elongation

Samples of polymers from the same polymerization run as those submitted for permeability studies were used to determine the mechanical properties (tensile modulus, per cent elongation, and ultimate elongation). These are presented in Figures 4 and 5.

Data were obtained in accordance with ASTM Method No. 1708 with a cross-head speed of 0.5 in./min, the gauge length 0.90 in., a chart speed of 20 in./min, 74°F, and a relative humidity of 53%.
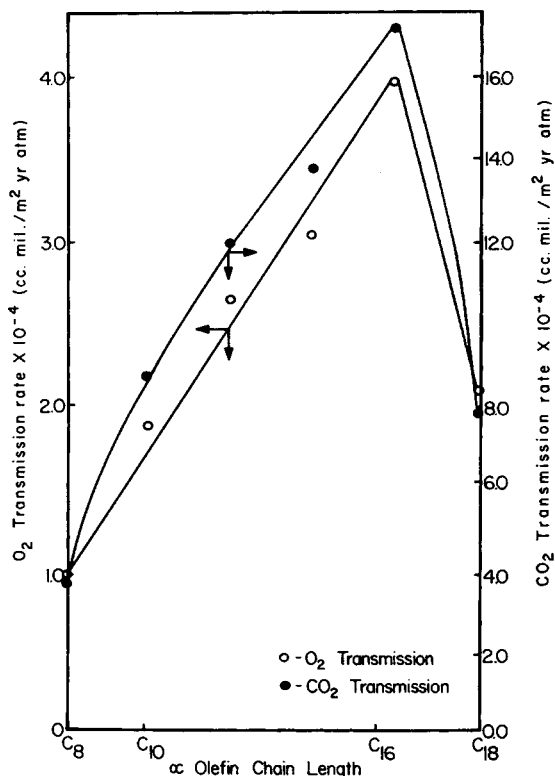
Fig. 3. Transmission rate vs. α-olefin chain length.

RESULTS AND DISCUSSION

It has been recognized that the olefin-SO_2 copolymers are not thermally stable and that thermal degradation occurs via an unzipping mechanism to yield mostly monomers. Mass-spectrometric thermal analysis indicates that the original comonomers are the only products of vacuum-pyrolytic degradation, and no other sulfur-containing products were found such as described by Naylor and Anderson.[8]

At higher temperatures under essentially flash pyrolysis conditions, the decomposition mechanism appears to be a chain-unzipping one to form the alpha-olefin and sulfur dioxide, followed by the pyrolysis of the alpha-olefin. An activation energy for degradation of approximately 46 kcal/mole is in line with a similar activation energy for pyrolysis of other chain-unzipping polymers such as polystyrene, variously reported from 55 to 70 kcal/mole, and poly(methyl methacrylate), a good average being 40 kcal/mole. Initiation of degradation is in the 175°C range, and pyrolysis is generally complete at 225°C with a heating rate of 20°C/min. It is noted that this value given for the activation energy is for the pyrolysis of the molten polymer, since the polymer melt temperatures for all of the polymers were well
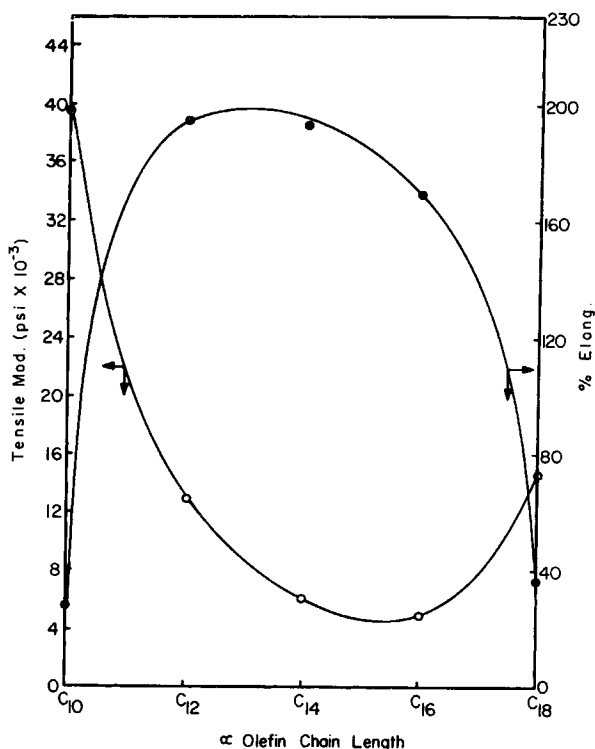
Fig. 4. Tensile modulus and per cent elongation vs. α-olefin chain length.

below their 175°C decomposition points. There is no real difference in the pyrolysis characteristics of the polymers as a function of chain length of the alpha-olefin comonomer. This is not unexpected since the rate-determining step must involve an endgroup initiation or a chain scission of a carbon–sulfur linkage. The alpha-olefin tail could be expected to play no great part in guiding the course of the pyrolytic reaction.

Variation of Properties of Function of Chain Length

In the series studied, the polysulfones prepared from the commercial olefins range from a hard, brittle material prepared from the C_6-alpha-olefin to an elastomer obtained from the C_{16}-olefin. It can be seen from Figure 5 that the permeabilities of oxygen and carbon dioxide reach a maximum at the C_{16}-based polymer. Also the tensile and elongation curves show a break at the C_{16}-polymer. In addition, the minimum density is obtained with the C_{16}-based polymer as shown in Figure 2. Our explanation for this behavior is that a plasticizing effect with the longer alpha-olefin chain is occurring since it can be shown that a C_{16} alpha-olefin can flexibilize a C_6-alpha-olefin-sulfone polymer. The plasticizing effect should become more efficient as the chain length of the alpha-olefin increases. However, we believe another effect occurs at C_{18}, specifically, side chain crystallization. In this case the
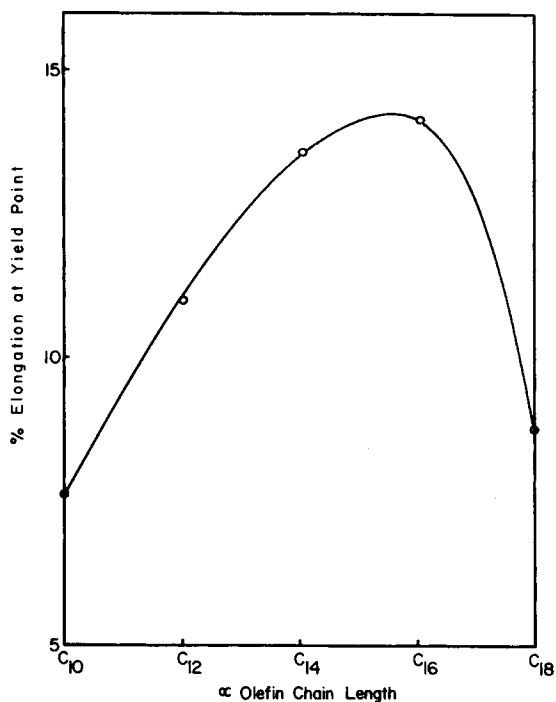
Fig. 5. Per cent elongation at the yield point vs. α-olefin chain length.

olefin side chain crystallizes independently of the backbone of the polymer, thus lowering its mobility and its plasticizing action on the main chain of the polymer. Side chain crystallization has been noted in several other homologous series of polymers. Overberger and co-workers[11] studied a series of poly(para-alkyl styrenes) with the normal aliphatic groups (C_2–C_{10}) substituted in the para position. They found a maximum in the glass transition temperature occurring with the C_{10} side chain. If one adds the length of a four-carbon unit for the approximate size of the para-phenylene moiety, then the total chain length would be similar to a C_{14} carbon chain rather than a C_{10} chain:
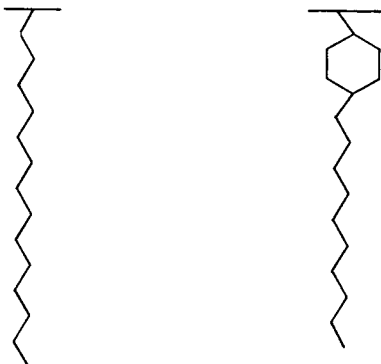
No direct evidence (x-ray data, etc.) was obtained for crystallinity in the polymers prepared. This does not rule out the proposed explanation for the variation in properties as function of chain length, since small-size crystallites cannot always be recognized in a polymeric matrix by x-ray analysis techniques. Purity of the monomer feed stock was ruled out as a factor for this variation since a similar trend was found for polymers prepared from highly purified monomers. The permeation data obtained from the terpolymer systems (Table I) also support this theory of competitive plasticization versus side chain crystallization as a causative factor for the maximum obtained for the physical properties.

TABLE I
Permeability of Terpolymers

Olefin[a]	O_2 transmission, cc-mil/m²-yr-atm	CO_2 transmission, cc-mil/m²-yr-atm
90 Hexene–10 hexadecene	1,860	6,870
90 Hexene–10 hexadecene (plasticized)[b]	4,340	
50 Hexene–50 hexadecene	9,960	49,630
16.7 Hexene–83.3 hexadecene	33,070	110,250
3.3 Hexene–96.7 hexadecene	37,530	142,300
16.7 Hexadecene–83.3 octadecene	34,730	154,700
50 Hexadecene–50 octadecene	46,700	191,900

[a] Figures before olefin indicate concentration in wt-%.
[b] Hexadecene, 10 wt-%, used as a plasticizer for the hexene–sulfur dioxide copolymer.

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