Note

Analysis of polycarbonate–polydimethylsiloxane block copolymers

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Block copolymers containing hard and soft segments form an important class of materials ranging from thermoplastics to thermoplastic elastomers depending on their composition and the size of the segments. Polydimethylsiloxane is an attractive soft segment in a block polymer, due to its thermal stability at elevated temperatures and high flexibility at low temperatures. The backbone not only has extremely useful thermal properties, but imparts outstanding weathering performance, and so is wide-ly used in conjunction, with harder blocks, for applications where durability is sought.

The properties of a wide range of block copolymers have been discussed in a general review by Noshay and McGrath[1]. Block copolymers containing polydimeth-ylsiloxane as the soft segment and various thermoplastics such as poly(α-methylsty-rene)[2], polystyrene[3] and polysulfone[4], as the hard segment, have been synthesized.

Characterisation of the surface composition of a series of polytetramethyl-*p*-silphenylenesiloxane–polydimethylsiloxane block copolymers has been investigated[5] using X-ray photoelectron spectroscopy and attenuated total reflectance Fourier transform infrared spectroscopy. The results show the surface region to be equivalent to the bulk composition of the copolymers. The use of gel permeation chromatogra-phy (GPC) has also been reported[6,7] for the determination of molecular weights and molecular weight distribution of polystyrene–polydimethylsiloxane block copoly-mers. Chromatography was carried out using a good solvent, toluene, whose refrac-tive index lies between those of the two components. In an earlier report[8], molecular weight data from GPC measurement was obtained using methyl ethyl ketone which is an adequate solvent for polydimethylsiloxane and a good solvent for polstyrene.

The morphology and mechanical properties of block copolymers containing bisphenol A [2,2-bis(4,4-hydroxyphenyl)propane] polycarbonate–polydimethylsilox-ane have been reported[5,9] together with structure–property relationships of copoly-mers with various stoichiometries. While a generalized chemical structure of the poly-mers is given in the literature, detailed chemical analysis has not been reported. A bisphenol A polycarbonate–polydimethylsiloxane block copolymer may be prepared using silylamine–hydroxyl reaction, *i.e.* by adding siloxane oligomers into a hydrated

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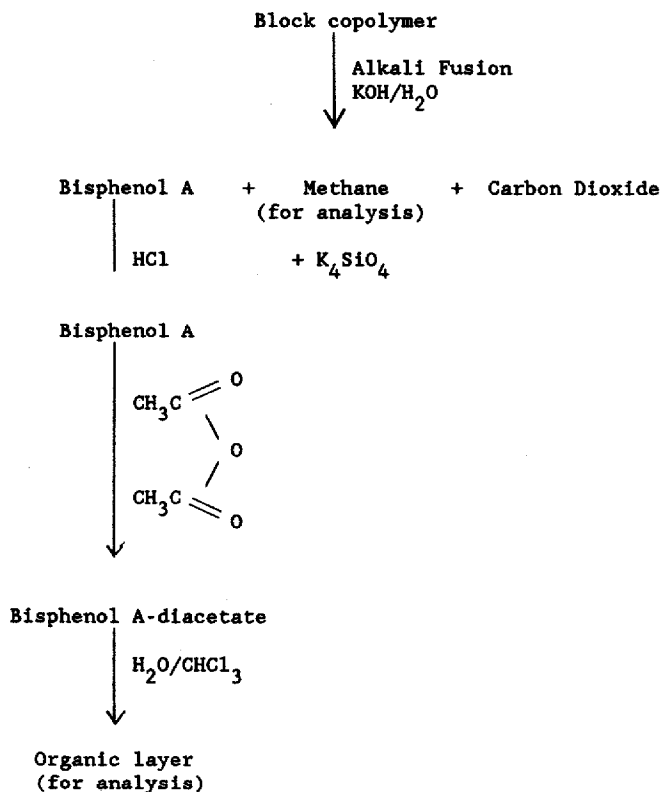[a] Permanent address: Ministry of Labour, Jakarta, Indonesia.

$$
\text{H[O-C}_6\text{H}_4\text{-}\underset{\underset{\text{CH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}\text{-C}_6\text{H}_4\text{-O-}\overset{\overset{\text{O}}{||}}{\text{C}}]_n\text{OC}_6\text{H}_4\text{-}\underset{\underset{\text{CH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}\text{-C}_6\text{H}_4\text{-OH}
$$

(A)

+

$$
(\text{CH}_3)_2\text{N[Si-O]}_m\text{Si-N(CH}_3)_2
$$

(B)

| Solvent (chlorobenzene)
↓ Heat

$[A\text{-}B]_m$ + $HN(CH_3)_2$

Fig. 1. Reaction involved during the preparation of bisphenol A polycarbonate–polydimethylsiloxane block copolymers.

solution of the bisphenol A polycarbonate in refluxing chlorobenzene. Fig. 1 shows a simplified scheme of the reactions which occur during the preparation of the block copolymer[9].

The polycarbonates are capable of hydrolysis and degradation of the copolymer may be carried out using alkaline fusion as has been extensively employed with a variety of condensation polymers[10].

This work describes the analysis using alkali fusion reaction–gas chromatography of bisphenol A polycarbonate–polydimethylsiloxane block copolymer. After cleavage, the bisphenol A fragment is identified as bisphenol A diacetate. The volatile reaction product (methane) corresponding to the methyl pendant groups of the dimethylpolysiloxane is determined using gas–solid chromatography. Acid fusion may also be used to cleave the copolymer, but prolonged digestion is required.

EXPERIMENTAL

Sample

A developmental sample of polycarbonate–polydimethylsiloxane block copolymer, provided by General Electric and with the trade name LR 3320 resin, was used for the analysis.

Alkali fusion procedure

About 200 mg of the sliced film sample were mixed with 13 g of the prefused potassium hydroxide–sodium acetate reagent[11]. The polymer–reagent mixture was heated in stainless-steel pressure tube fitted with a serum cap at 250°C for 1–2 h. The reactant gas in the tube was used for the analysis of methyl pendant groups of the polydimethylsiloxane block by injecting about 0.5 ml of gas into the gas chromatograph.

Block copolymer

| Alkali Fusion
| KOH/H$_2$O
▼

Bisphenol A   +   Methane   +   Carbon Dioxide
              (for analysis)

| HCl   + K$_4$SiO$_4$

Bisphenol A

$$CH_3C \overset{\diagup}{=} O$$
$$\diagdown$$
$$O$$
$$\diagup$$
$$CH_3C \overset{\diagdown}{=} O$$

▼

Bisphenol A-diacetate

| H$_2$O/CHCl$_3$
▼

Organic layer
(for analysis)

Fig. 2. Analytical scheme.

For the analysis of bisphenol A, the tube was allowed to cool to room temperature. The tube was then opened and the contents were transferred to a beaker followed by the addition of sufficient hydrochloric acid solution to effect neutralization. After evaporation to dryness, an excess of acetic anhydride (5 ml) and about 0.5 ml of 1-methylimidazole were added. The 1-methylimidazole facilitates complete acetylation of the difunctional alcohol. The mixute was refluxed for 1 h to ensure the formation of the bisphenol A diacetate. After cooling, the mixture was transferred to a separating funnel containing 25 ml of water to destroy the excess of reagent and dissolve the salt. The bisphenol A diacetate was recovered by extraction using 20-ml aliquots of chloroform, and the combined chloroform solution was dried over anhydrous magnesium sulphate. Finally, the solution was concentrated under reduced pressure to about 1 ml for gas chromatographic analysis. The analytical scheme is shown in Fig. 2.

Gas chromatography

Gas chromatography employed a Hewlett-Packard 5750 research instrument with flame ionization detection. Helium was used as carrier gas with a flow-rate of 60 ml/min. Bisphenol A diacetate was separated on a 12 ft. × ¼ in. O.D. aluminium column packed with 5% (w/w) neopentylglycol succinate on Chromosorb W DMCS. The column was operated isothermally at 218°C.

Separation of the volatile reaction product was carried out on a 6 ft. × ⅛ in. O.D. stainless-steel column, packed with Porapak Q and operated isothermally at 52°C.

RESULTS AND DISCUSSION

The polycarbonate–polydimethylsiloxane block copolymer sample was successfully cleaved using alkali fusion. The bisphenol A fragment was converted to bisphenol A diacetate to allow examination by gas chromatography. The methane fragment was identified by gas–solid chromatography on a Porapak Q column, similarly to the determination of organic pendant groups on the siloxane intermediate in silicone polyester resins, as previously reported[12,13].

The separation of bisphenol A diacetate, as shown in Fig. 3, was conducted using a polar-neopentylglycol succinate column, as previously used for vinyl esters[14]. A chromatogram showing the separation of the methane fragment from the polydimethylsiloxane block is shown in Fig. 4.

It is apparent that carbon dioxide is a product of the reaction, as shown in Fig. 2. While carbon dioxide is readily detected, its measurement in this analysis is poor due to its ready reaction with the large amount of potassium hydroxide present. The carbon dioxide might be liberated from the protassium carbonate and estimated but such an assay is of limited value as the initial fusion reagent contains small but variable amounts of potassium carbonate depending on its history. Some ionisation detectors respond poorly to carbon dioxide and thermal conductivity detection is indicated.

Acid fusion procedures have been proposed as a preferable method for the analysis of polyol and carboxylic acid contents in silicone polyester resins. However, the procedure could not be applied for the analysis of glycerol, bisphenol A and methacrylic acid in vinyl ester resin systems[14]. It was proposed that the resistance of vinyl ester resins to cleavage through hydrolysis catalysed by acid fusion reagents is due to the particular structure of the resin and the presence of bisphenol A. Similarly, polycarbonate–polydimethylsiloxane block copolymers contain bisphenol A and do
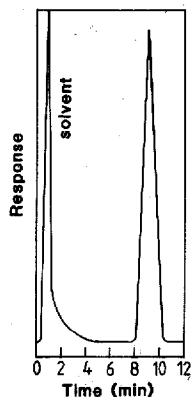

Fig. 3. Gas chromatogram showing the separation of bisphenol A diacetate.
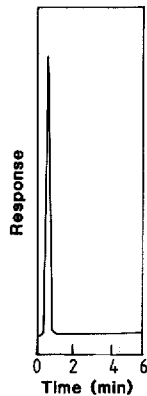
Fig. 4. Gas chromatogram showing the separation of methane.

not contain any ester linkages. However, a prolonged digestion (more than 24 h) using *p*-toluenesulphonic acid–acetic acid was found to cleave the block copolymer. Methyl pendant groups in the polydimethylsiloxane block could also be analysed using the acid fusion reaction procedure as previously described[12,13]. Alkali fusion is more efficient than acid fusion, the complete analysis requiring 1–2 h.

Analysis of polyol, carboxylic acid and silicate fragments has been achieved simultaneously with silicone polyesters[15]. The fragments were identified as their trimethylsilyl derivatives after alkali fusion of the silicone polyester resins. Silylation of the fragments after alkali fusion of the polycarbonate–polysiloxane block copolymers could also be applied, and similar results would be obtained, *i.e.* with the addition of silyl derivative of silicate fragment.

Alkali fusion reaction–gas chromatography has been demonstrated to be a simple method for the analysis of block copolymers containing bisphenol A polycarbonate–polydimethylsiloxane, and thus could be widely used for other block copolymers.

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