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Preparation and Thermal Properties of Block Copolymers of PDMS with Styrene or Methyl Methacrylate using ATRP

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Abstract

This note describes the synthesis of A-B-A block copolymers with B = PDMS and A = polystyrene or PMMA. The method involves the use of chloromethyl terminated polysiloxanes as initiators for ATRP. Characterisation of the copolymers by NMR is described together with their thermal properties as measured by DSC.

Keywords: Block copolymers; PDMS-Styrene; PDMS-PMMA; ATRP.

INTRODUCTION

There is tremendous current interest in the preparation of polymers and copolymers with organic and inorganic segments¹. In addition to the synthetic challenge posed, they are finding application in, for example, the preparation of composite materials. Perhaps the most widely used series of inorganic backbone polymers is the siloxanes, $(RR'SiO)_n$ and this has led to efforts to exploit their unique properties in copolymers with organics such as acrylic monomers. The most usual methods² for producing these materials employs anionic polymerization of the organic block to the required chain length and subsequent use of the polymer anion to initiate polymerization of the dimethyl siloxane trimer or tetramer. A second approach uses hydride terminated siloxanes to react with vinyl terminated organics in a hydrosilylation reaction.

A recent advance in the controlled synthesis of polymers has been the development of Atom Transfer Radical Polymerization, ATRP. This involves the use of an alkyl halide initiator in conjunction with a transition metal complex. The principle³ of ATRP is that the complex, for example copper I bromide with bipyridyl, maintains an equilibrium between free polymer chains with active radical chain ends and complexed polymer chains. This ensures a low concentration of active radicals, minimising termination reactions. This allows “living” conditions to be maintained during a radical polymerization so that materials with controlled molecular weight and polydispersity can be controlled.

In an early example, Matyjaszewski et al.⁴ used 1-phenylethyl chloride as an initiator for the polymerisation of styrene, with CuCl complexed by 2,2'-bipyridyl (bipy) as a promoter for the chlorine atom transfer. Polydispersities less than 1.5 were obtained and Matyjaszewski coined the term ‘Atom Transfer Radical Polymerisation’ (ATRP) to describe this method of radical “living” polymerisation. Many advances in the technique have been made in recent years and it has been applied to a range of monomers and shown to be a useful technique under a variety of conditions.⁵

The preparation of block copolymers using ATRP has also been demonstrated. A homopolymer containing a halide-terminated chain end is used as an initiator for the ATRP of a second, different, monomer. If the initiator is only functionalised at one chain end, an AB-type block copolymer results. If it is functionalised at both ends, an ABA-type block copolymer will be produced. This technique has been used to create copolymers of polyTHF with styrene, methyl acrylate and methyl methacrylate.⁶ Matyjaszewski and co-workers^{7,8} have reported the use of functionalised siloxane chains for producing block and graft copolymers of styrene and other vinyl monomers, including acrylates and methacrylates.

Haddleton and co-workers⁹ recently reported briefly on an alternative method whereby amino terminated PDMS was functionalised and used to prepare copolymers with (dimethylamino)ethyl methacrylates. Similar materials have been produced by Banez et al.¹⁰ using alternative initiation methods. Lutsen and co-workers¹¹ showed that block copolymers of styrene with other silicon containing polymers could be produced by ATRP when they successfully used a bipyridyl complexed copper (I) bromide as a catalyst for ATRP of styrene onto the end of chains of poly(methyl phenyl silane). This opens an alternative route to acrylic-organosilane polymers with controlled structure and functionality. Their method required a poly(organosilane) to be end capped with chloromethylphenyl groups which acted as an initiator.

This note presents a preliminary report of the use of related chemistry for the preparation of A-B-A block copolymers where B = PDMS and A = styrene or methyl methacrylate and of their thermal characterisation by DSC. A PDMS chain is end-functionalised with chloromethyl styrene and acts as an initiator for polymerization of the vinyl monomer.

EXPERIMENTAL

Analytical methods

Infra-red spectroscopy was carried out on a Perkin-Elmer 983 IR spectrophotometer. Samples were analysed as films cast onto NaCl plates from CHCl₃. Samples for NMR analysis were dissolved in CDCl₃ (~50 mg in 1.5 cm³) and spectra recorded using either a JEOL GX270 FT-NMR, or a GX400 FT-NMR. TMS was used as an internal standard except where the siloxane integrals were required, when an external TMS standard was used. ¹H, ¹³C and ²⁹Si NMR were recorded. Differential scanning calorimetry, DSC, was carried out on a TA instruments 2910 calorimeter. Aluminium pans were employed with an empty pan of equal mass used as the reference. Temperature calibration was achieved using water and indium standards.

Materials

Hydride-terminated PDMS with approximate molecular weights 580 and 5770 were used as received from Dow Corning. Solvents and reagents were obtained from Aldrich Ltd and dried and purified by standard methods. Styrene and methyl methacrylate were obtained from

Aldrich Ltd. and inhibitors removed before use by washing with 10% sodium hydroxide and water followed by distillation under reduced pressure.

Synthesis of the ATRP initiator 1

60 μL of a 0.24 wt% solution of chloroplatinic acid (H_2PtCl_6) in 2-propanol (IPA) and 0.9789 g of (chloromethyl)styrene (CMS) were charged to a 50 cm^3 flask fitted with a pressure equalising dropping funnel, containing 1.86 g of hydride-terminated PDMS ($M_n \sim 580$). The molar ratio of the CMS to the hydride-terminated PDMS was 2:1, while 5×10^{-5} equivalents (based on the CMS) of the catalyst were used.

The hydride-terminated PDMS was added over 2.5 hours under a positive pressure of nitrogen gas. After 1 hr and 2 hr, the solution was heated gently with a hot air gun for approximately 5 min. The solution was stirred for a total of 3 hours after which time the solvent was removed by heating to 60°C under vacuum. The reaction was monitored by following the loss of the Si—H peak in the infra-red spectrum at 2125 cm^{-1} . The product was then filtered through a 0.2 μm membrane filter to remove any particulate matter and leave the end-functionalised PDMS which was dried in vacuum at 70°C for 48 hours. The yield of the final product ranged from 60 to 80%.

^1H NMR (ppm, CDCl_3): 7.3 m (aromatic ring), 4.7 s (CH_2Cl), 2.8 m (PhCH_2), 2.3 q (PhCH), 1.5 m (CH_3), 1.0 m (SiCH_2), 0.2 m (SiCH_3).

Synthesis of the longer chain initiator, 2

The same method was used except that 30 μL of the chloroplatinic acid solution and 0.5290 g of CMS were used to give the same molar ratios. In this case, stirring at 50°C for a 24 hr was necessary for reaction, again indicated by the loss of the Si—H band in the infra-red spectrum. The final yield of product **2** obtained was 90 %. The ^1H NMR was similar to that of **1** with integrals reflecting the higher proportion of siloxane in the compound.

Preparation of PDMS copolymers

0.5 g **1**, 0.112 g freshly reprecipitated copper (I) chloride, 0.353 g 2,2'-bipyridyl (bpy), 6.5 cm^3 styrene and 6.5 cm^3 *o*-xylene were charged to a dry flask. The molar ratio of **1**:CuCl:bpy: styrene used was 1:2:4:100. The flask was sealed under dry nitrogen and heated to 130°C . After 3 - 5 hr, the flask was cooled to room temperature and 20 cm^3 of toluene added before filtration. The copolymer was precipitated into ice-cold methanol and purified

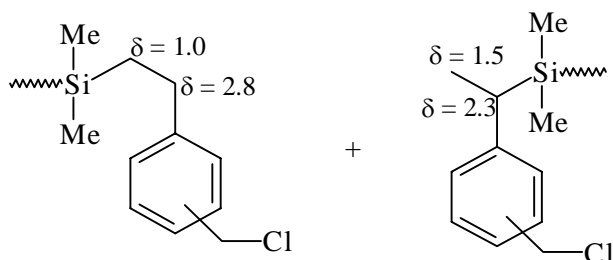
by re-precipitation from toluene and drying overnight in vacuum at 60°C. The recovered polymer was a viscous, cloudy oil suggesting that it was a phase separated material.

The reactions using MMA rather than styrene were conducted in the same manner with the same molar ratios of monomer. Reactions using the longer chain PDMS block, **2**, were conducted using the same methods except that 3.4 g of the PDMS were used and the reaction allowed to proceed for 5 hr.

RESULTS AND DISCUSSION

Synthesis of initiators

The reaction sequence for the preparation of the functionalised PDMS blocks is shown in Scheme 1 and involves hydrosilylation of vinyl benzyl chloride onto hydride terminated PDMS. The ^1H nmr spectrum of the compound **1** is shown in Figure 1 and clearly indicates that hydrosilylation occurs at both ends of the vinyl double bond. The nmr data show that the isomer with the free methyl group constitutes ~35% of the total. The reactivity of the chloromethyl group would be expected to be similar in both cases so that the mixture was used without further purification.



1 contains only 7 siloxane repeat units so that to contrast the behaviour with that of a longer chain, a second initiator, **2**, was prepared using the same method but starting with a hydride-terminated PDMS of $M_n = 5770$, giving approximately 77 Me₂SiO units. The same spectra, allowing for the compositional difference, were obtained.

Synthesis and characterisation of block copolymers with styrene

Copolymerisation of **1** with styrene was conducted according to the reaction shown in Scheme 2. IR and ^1H NMR spectroscopy of the recovered polymer, **3**, clearly showed that the PDMS-Styrene copolymer had been produced as expected. However, from the NMR, the material was found to contain approx. three times as much styrene as the 50 repeat units expected from the mole ratios used in the reaction. It therefore seems that only a proportion

of the initiator was active in the polymerization. The theoretical mole ratio can only be produced when the initiator acts efficiently in the halogen transfer.¹² In contrast, reaction of **2** with styrene to give copolymer **4**, yielded a polymer with less styrene than expected. This suggests that there is some difference in efficiency between the two initiators but more work is needed to clarify this situation. The catalyst system used was only poorly soluble in the reaction medium and this may have played a part in the differences between the systems.

Given that the polymerisation was conducted at 130°C, it is important to rule out the possibility of 'conventional' free radical polymerisation taking place to form polystyrene homopolymer. The reactions were repeated with the omission of the PDMS initiator. No homopolymer was formed so the presence of the CuCl/bpy complex appears to completely inhibit the thermal polymerisation of styrene in the absence of a chloromethyl ligand.

Figure 2 shows the DSC traces obtained from the copolymers, homo-polystyrene and homo-PDMS ($M_n \approx 3000$). The characteristic T_g of polystyrene at 105°C is evident as are the PDMS values of approx. -125°C, for T_g and the melting exotherm around -50°C. In the DSC of **3** (the short PDMS block), there is a change of slope centred around 85°C together with a transition at 100°C. It therefore appears that the T_g of the styrene blocks is lowered somewhat by the presence of the flexible PDMS block in the middle of the copolymer. As expected from the small amount of PDMS in the polymer, transitions associated with this segment of the copolymer are barely discernable. In the case of copolymer **4** with a much longer PDMS block, the T_g of the polystyrene is just visible at ~80°C, again somewhat lower than the homopolymer as has been observed previously¹³. The melting temperature of the PDMS block at ca. -50°C is very clear as a consequence of the much longer PDMS block. This is characteristic of a phase separated morphology of the copolymer.

Synthesis and characterisation of block copolymers with methyl methacrylate

The same methods employed with styrene was used with **1** and **2** as initiators for ATRP of MMA, again aiming to produce an ABA-type triblock copolymer with each PMMA block having ~50 repeat units.

The IR and ¹H NMR spectra were clearly consistent with those expected for the copolymers. As with the ATRP with styrene, the copolymer **5** (the shorter PDMS block) contained a higher ratio of MMA: siloxane than expected from the composition of the reaction mixture. Approx. 80% more MMA was incorporated into **5** and ~20% into **6** (the longer PDMS block) again indicating some inefficiency of the initiator. It is clear that, for optimum reaction, alternative ligands and/or end groups must be used⁸.

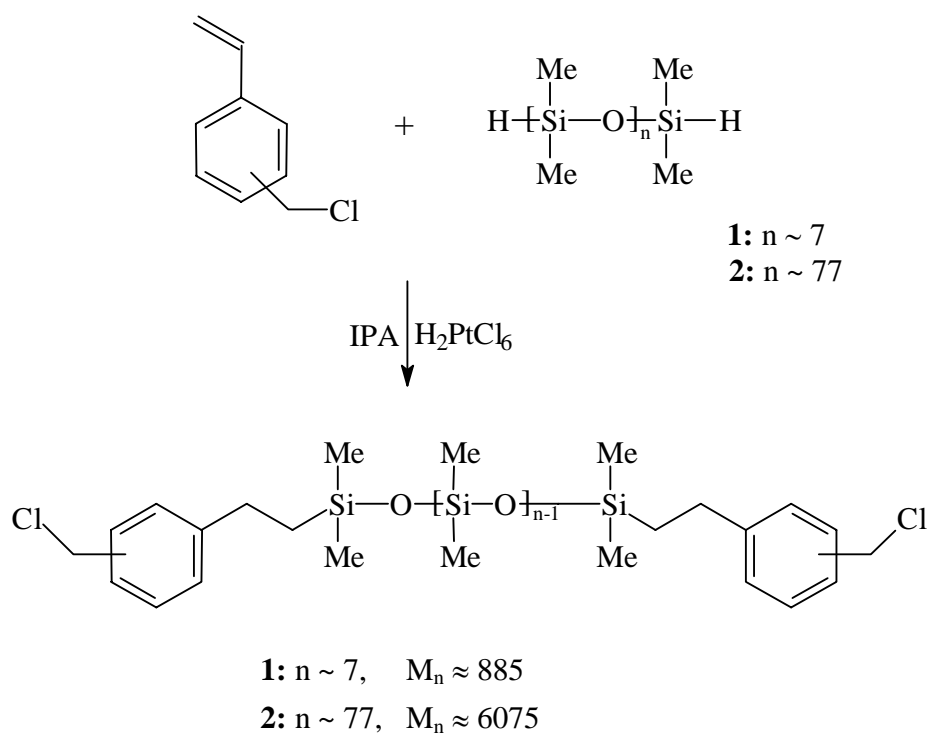
The DSC thermograms of the poly(PMMA-DMS-PMMA) are shown in Figure 3. The T_g of PMMA is at ~ 110°C. In copolymer **5** it is much lower at ~25°C. The inclusion of the short PDMS block seems to have a considerable plasticisation effect on the PMMA blocks. In this case, properties of the PDMS segment are not observable. Where the longer PDMS block is incorporated, the T_g and melting exotherm of the siloxane segments is visible and occur at substantially the same temperature as in the homopolymers. The T_g of the PMMA segments appears to be rather lower. A larger shift in T_g is noticed than with polystyrene copolymers indicating that the phase morphology is different. This is under further investigation.

CONCLUSIONS

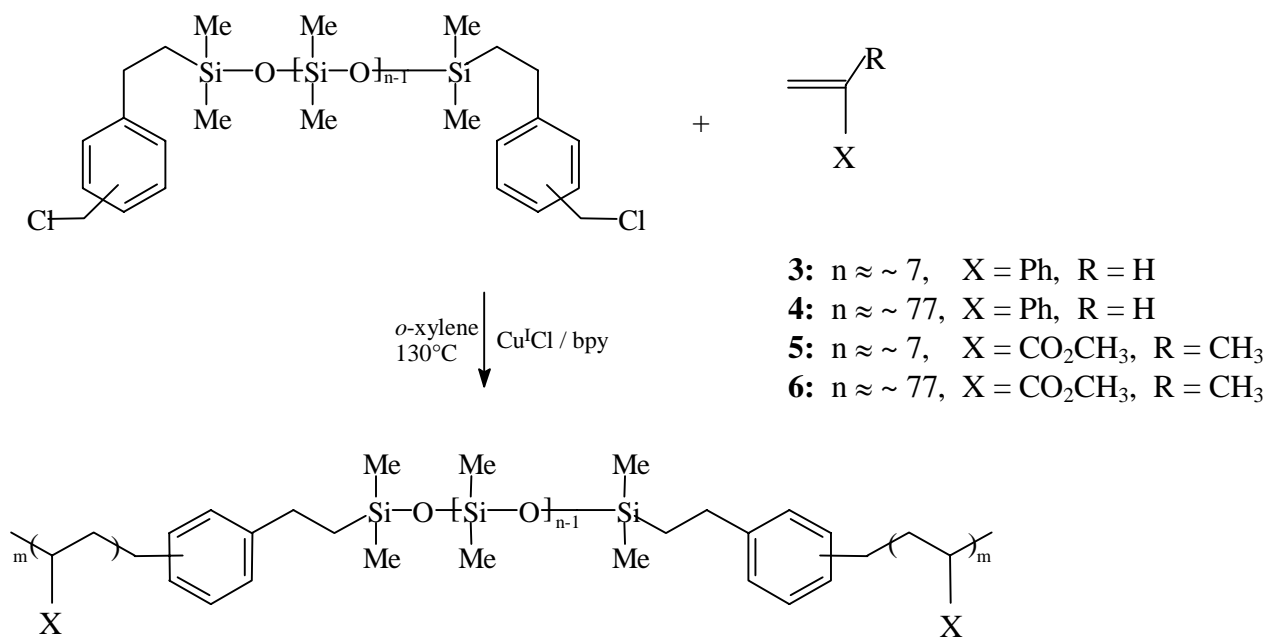
ATRP has been employed successfully to produce copolymers of PDMS with polystyrene and PMMA. Two siloxane-based, chloromethyl terminated initiators, with differing chain lengths were used to initiate the polymerizations to form ABA-type materials. The copolymers produced using ATRP displayed interesting thermal behaviour which requires further investigation. Further work is underway to clarify these effects.

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Scheme 1. Production of functionalised PDMS ATRP initiators



Scheme 2. ATRP synthesis of PDMS block copolymers

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CAPTIONS FOR FIGURES

Figure 1. ^1H NMR spectrum of the ATRP initiator, **1**

Figure 2. DSC thermograms of PDMS-Styrene block copolymers
(a) PDMS; (b) Polystyrene; (c) copolymer **3**; (d) copolymer **4**.

Figure 3. DSC thermograms of PDMS-PMMA block copolymers
(a) PDMS; (b) PMMA; (c) copolymer **5**; (d) copolymer **6**.

Figure 1.

