It is evident from the study of the conductivity of the model system consisting of a mixture of organic liquids, dimethoxyethane and propylene carbonate, that this defines the upper limit of a totally organic system as 10^{-2} Ω^{-1} cm^{-1} at 25 °C. Replacement of dimethoxyethane by an amorphous cross-linked PEO matrix, with only the loss of 1 order of magntidue, is remarkable. In all probability a further increase in conductivity may be possible and a value of 5×10^{-3} Ω^{-1} cm^{-1} is foreseen.

The work described in this paper is featured in a European patent[19] and copending applications in the USA and elsewhere.

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Registry No. 1, 124604-86-0; 2, 88752-55-0; 3, 64786-16-9; 4, 124604-87-1; 5, 124618-70-8; 6, 115401-75-7; 7, 124604-88-2; 8, 124604-89-3; 9, 115383-11-4; 11 (homopolymer), 124618-72-0; PC, 108-32-7; DME, 110-71-4; NMP, 872-50-4; $\mathrm{LiSO_3CF_3}$, 33454-82-9; (dibutyl carbonate)(diethyl glycol) (copolymer), 124604-90-6; methacrylic anhydride, 760-93-0.

Group-Transfer Polymerization on a Polymeric Support

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ABSTRACT: Three silyl ketene acetals (**4**, **7**, and **9**) bonded to cross-linked polystyrene beads were synthesized from chloromethylated polystyrene. Suspensions of these supported silyl ketene acetals in tetrahydrofuran (THF) containing methyl methacrylate (MMA) and anion catalysts for group-transfer polymerization (GTP) gave rapid formation of graft polymers, almost without formation of ungrafted, soluble PMMA. Initiation of the GTP of MMA with **7** in acetonitrile gave insignificant chain transfer to solvent. Initiation of the GTP of acrylonitrile with **9** at −50 °C gave quantitative conversion to graft copolymer, while initiation at room temperature gave soluble poly(acrylonitrile) as well. In contact with gaseous MMA or acrylonitrile, catalyst-doped **4** was converted to graft copolymer. The GTP of MMA in THF solution in the presence of cyanomethyl-substituted cross-linked polystyrene beads (**1**) gave a graft copolymer as a result of chain transfer.

Introduction

The success of the Merrifield peptide synthesis on polymeric supports[1] and the growing importance of surface modification by graft polymerization led us to investigate the potential of group-transfer polymerization (GTP)[2] on polymeric supports. In principle, techniques analogous to those for the synthesis of peptides could be used for the construction of highly designed addition polymers, taking advantage of the living nature of GTP. In this paper we report the synthesis of several kinds of silyl ketene acetals on cross-linked polystyrene and their use in initiation of GTP of acrylic monomers. Objectives were to gain insight into chain-transfer processes in GTP through the use of supported initiators and chain-transfer agents and to obtain mechanistic information on the GTP of acrylonitrile, a monomer that is difficult to study because of its high propagation rate. DNA-binding studies using graft copolymers prepared by these techniques will be reported elsewhere. Otsu and co-workers have described the successful grafting of polystyrene and poly(methyl methacrylate) onto cross-linked polystyrene containing dithiocarbamate groups by use of a free radical photoiniferter technique.[3]

[†] Contribution No. 5002.

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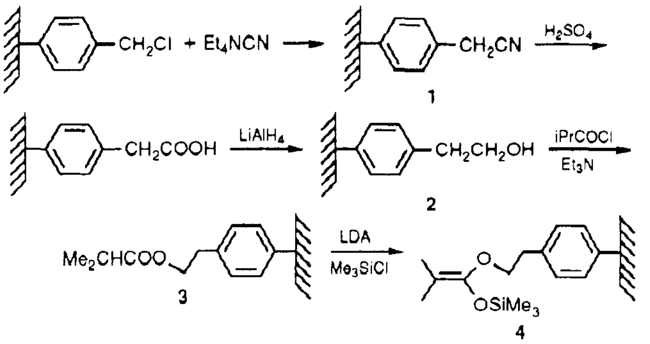
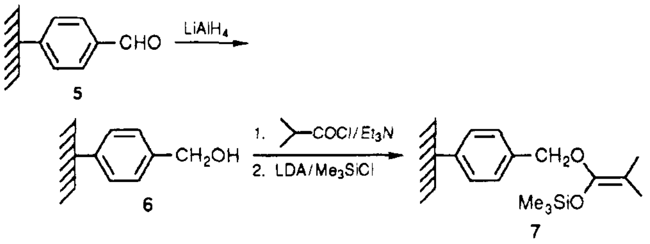
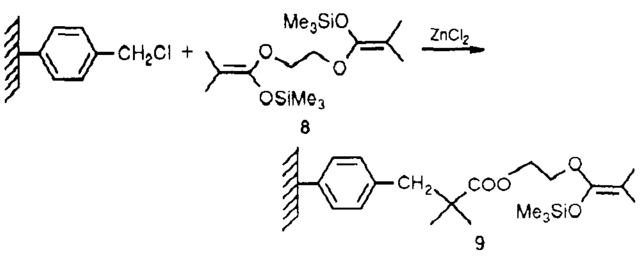
Scheme I



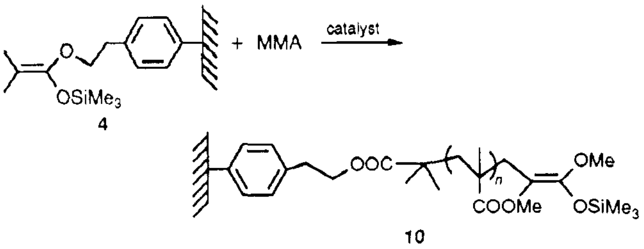
Scheme II



Scheme III



Scheme IV



Results and Discussion

Synthesis. Chloromethylated polystyrene (200–400 mesh beads, cross-linked with 1% divinylbenzene, 4.09 mequiv/g of Cl) was converted to β-hydroxyethyl-substituted polystyrene by a modification of the method of Darling and Frechet[4] (Scheme I). The poly[(chloromethyl)styrene] was converted to poly[(cyanomethyl)styrene] (1) with tetraethylammonium cyanide in acetonitrile/THF. Acid hydrolysis of 1 to (carboxymethyl)polystyrene and subsequent reduction with lithium aluminum hydride gave (β-hydroxyethyl)polystyrene (2). Reaction with isobutyryl chloride and triethylamine gave the corresponding isobutyric ester 3. Treatment of 3 with lithium diisopropylamide and chlorotrimethylsilane at −78 °C gave the supported silyl ketene acetal 4 with a loading of 2.4 mequiv of silicon per gram of polymer. Infrared analysis confirmed the presence of the silyl ketene acetal carbon–carbon double bond with the presence of absorption at 1702 cm^{-1}. Absorption at 1730 cm^{-1} showed the presence of some ester 3.

A polystyrene-supported silyl ketene acetal 7 with one less methylene spacer was synthesized (Scheme II) from formyl-substituted cross-linked polystyrene (5) (obtained by dimethyl sulfoxide oxidation of chloromethylated polystyrene according to Frechet and Hacque[5]). The aldehyde 5 (1.3 mequiv/g) was reduced with lithium aluminum hydride to (hydroxymethyl)polystyrene (6), which was converted to the isobutyrate and then to the silyl ketene acetal 7 with a loading of 0.8 mequiv of silicon per gram of polymer. IR analysis of 7 showed peaks of nearly equal intensity corresponding to silyl ketene acetal C=C (1705 cm^{-1}) and ester C=O (1735 cm^{-1}).

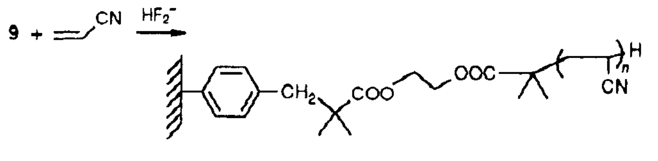
A one-step synthesis of polystyrene-supported silyl ketene acetal (Scheme III) was achieved by the zinc chloride catalyzed reaction of excess 1,2-bis[[1-(trimethylsiloxy)-2-methyl-1-propen-1-yl]oxy]ethane 8 with chloromethylated polystyrene (1% cross-linked with divinylbenzene, 1.4 mequiv/g of chlorine) to give 9 with a loading of 0.66 mequiv of silicon per gram of polymer. Replacement of all of the chlorine of the starting material was not possible, and residual chloromethyl groups (0.33 mequiv/g) remained in 9. IR analysis showed the presence of the characteristic 1705-cm^{-1} band for silyl ketene acetal as well as a 1730-cm^{-1} ester C=O band.

Initiation Studies. When a stirred suspension of polystyrene-supported silyl ketene acetal 4, 7, or 9 in tetrahydrofuran (THF) was treated with MMA and a GTP anion catalyst[6] (such as $TASHF_2$ or tetrabutylammonium *m*-chlorobenzoate), exothermic polymerization of the MMA occurred at a rate that appeared to be slower than that typical of the GTP of MMA under homogeneous reaction conditions. The reaction product, isolated by filtration, was a graft polymer of MMA on polystyrene. Initiation of GTP of 2 g of MMA with a suspension of 1 g of 4 (2.4 mequiv/g) in 15 mL of THF occurred upon dropwise addition of a solution of tetrabutylammonium *m*-chlorobenzoate (0.04 mmol) in THF (Scheme IV). In 20 min the temperature rose 13 °C. After 60 min, NMR analysis of the supernate showed that all of the MMA had reacted and that no PMMA was dissolved in the solution. Thus, only grafting to the cross-linked polystyrene beads had occurred giving 10, and no chain transfer to soluble species was detected. Filtration of the product followed by extraction in a Soxhlet apparatus with THF gave 98% yield of graft copolymer. IR analysis of the product showed the presence of large amounts of grafted PMMA. Although the polymer beads had increased in mass 3-fold, they retained their original spherical form.

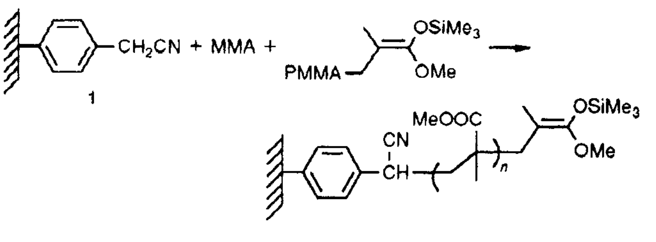
Initiation of GTP of neat MMA (15 mL) with 1 g of 9 (0.71 meq/g) in the presence of tetrabutylammonium *m*-chlorobenzoate catalyst[10] resulted in more than a 4-fold increase in the mass of the supported initiator to 4.23 g during a period of 3 h. The entire reaction mixture solidified due to swelling of the resulting graft copolymer by MMA.

Bandermann and co-workers[7] have reported a termination reaction in GTP of MMA in acetonitrile solution that results from silylation of acetonitrile by the silyl ketene acetal end group. The absence of significant chain transfer[8] to acetonitrile was demonstrated by initiation of the GTP of MMA with supported silyl ketene acetal 7 in 4:1 THF–acetonitrile in the presence of tetrabutylammonium *m*-chlorobenzoate. The yield of isolated graft copolymer was 94%, and only 0.75% of the polymerized MMA was isolated from solution. The trace of polymer

Scheme V



Scheme VI



formed in solution may have resulted from chain transfer to acetonitrile. Our experiment shows that initiation of new polymer chains by any silylated acetonitrile species[7] formed during the GTP of MMA in acetonitrile solution is insignificant.

Initiation of GTP of 10 mmol of acrylonitrile (AN) with 1 g of supported silyl ketene acetal **9** (0.66 mequiv/g) and TASHF$_2$ in dimethylformamide (DMF) at -50 °C gave conversion of all of the AN to graft copolymer (Scheme V). No residual monomer nor polyAN were detected in solution. Although this experiment confirms that all of the polyAN resulted from initiation by the silyl ketene acetal without chain transfer, it does not prove that the silicon remained associated with the growing end of the polymer during propagation. When the experiment was carried out at 25 °C, conversion was incomplete, and 42% of the polyAN was isolated from solution while the remainder was grafted to the support. This shows that an important side reaction in the GTP of AN[2b] is chain transfer to monomer. At -50 °C this chain transfer is suppressed. Thus, GTP of AN bears a strong resemblance to anionic polymerization of AN.[9]

In addition to initiation of GTP of monomers in solution, polymer-supported silyl ketene acetals can also be used to initiate GTP of monomers introduced from the gas phase. The supported initiator **4** was first treated with a solution of tetrabutylammonium *m*-chlorobenzoate in THF and dried for 24 h at room temperature, and then the catalyst-doped polymer was exposed to the vapor of MMA in a drybox for 24 h. After drying of the polymer at 25 mTorr, the weight increase due to formation of grafted PMMA was 125%. Only 0.4% of the PMMA could be extracted with THF. A similar experiment with gaseous acrylonitrile gave a 10% increase in weight due to formation of grafted poly(acrylonitrile). Chain termination appears to be much more important with a slow monomer feed of AN than with a slow monomer feed of MMA.

In earlier work[8] it was found that arylacetonitriles are efficient chain-transfer agents for GTP in the presence of anion catalysts. When GTP of MMA was carried out in the presence of suspended cross-linked polystyrene beads containing cyanomethyl groups **1** (4 mequiv/g, Scheme VI), 54% of the charged monomer was isolated from solution as PMMA ($\bar{M}_n$ = 5240, $\bar{M}_w$ = 9070, $\bar{M}_w/\bar{M}_n$ = 1.73), and PMMA was grafted to the supported chain-transfer agent resulting in a 260% weight increase. About 5% unpolymerized MMA was detected by NMR analysis. GPC analysis of the soluble PMMA showed a pronounced low molecular weight tail. The PMMA isolated from solution accounts for 53% of the initiator, so about 47% of the silicon of the initiator was captured by the support. The theoretical $\bar{M}_n$, assuming no chain transfer, is 4850 (after correcting for 95% conversion). Since the measured $\bar{M}_n$ is much higher than the theoretical $\bar{M}_n$, we can conclude that the rate of capture of silicon by the support from initiator and small oligomers is much greater than the rate of capture from living polymer.

Conclusions. Silyl ketene acetals bonded to an insoluble cross-linked polymeric support initiate the GTP of MMA in a more or less normal fashion to form graft copolymers. Graft copolymers are also obtained by chain transfer to cross-linked cyanomethylated polystyrene. Initiation of the GTP of AN with a supported silyl ketene acetal leads to polyAN grafts. An important side reaction at room temperature is chain transfer to monomeric AN.

Experimental Section

Materials and Methods. THF was distilled from sodium and benzophenone immediately prior to use. Dichloromethane was dried over 4-Å molecular sieves. *N,N*-Dimethylformamide and dimethyl sulfoxide were distilled thorugh a Vigreux column under reduced pressure. Acetonitrile (<0.0005% water), anhydrous triethylamine, and anhydrous diisopropylamine were used as purchased from Aldrich Chemical Co. Silylation grade chlorotrimethylsilane was purchased from Petrarch Systems. Chloromethylated beads (200–400 mesh) of polystyrene cross-linked with 1% divinylbenzene (activities 4.2 and 1.4 mequiv/g) were purchased from Bio-Rad Laboratories. Silyl ketene acetals,[2b] GTP catalysts,[2b,6] and tetraethylammonium cyanide[10] were prepared as described earlier. ^{1}H NMR spectra were recorded with a Nicolet 360WB spectrometer.

(Cyanomethyl)polystyrene (1). A mixture of 8 g of tetraethylammonium cyanide and 9 g of (chloromethyl)polystyrene (4.09 mequiv/g) in 90 mL of acetonitrile and 35 mL of THF was stirred at 50 °C for 18 h under an argon atmosphere. (Cyanomethyl)polystyrene, isolated by filtration under nitrogen, was washed with 3:1 acetonitrile–water and with THF and extracted with THF in a Soxhlet apparatus for 18 h. IR: 2245 cm^{-1} (CN). Anal. Calcd for $(C_{10}H_{10})_{0.01}(C_8H_8)_{0.49}(C_{10}H_9N)_{0.50}$: C, 87.42; H, 6.93; N, 5.65; Cl, 0. Found: C, 86.11; H, 7.19; N, 5.75; Cl, 0.19.

[2-(Isobutyryloxy)ethyl]polystyrene (3). To a stirred mixture of 75 mL of dichloromethane, 5.6 mL (40 mmol) of triethylamine, and 5 g (20 mequiv) of (hydroxyethyl)polystyrene (**2**) (prepared from (cyanomethyl)polystyrene via hydrolysis to the carboxylic acid and reduction with lithium aluminum hydride by the procedures of Darling and Frechet[4]) was added 4.2 mL (40 mmol) of isobutyryl chloride. After 18 h, the polymer was collected by filtration and washed with dichloromethane, water, and THF. The product was extracted with sodium-dried THF in a Soxhlet apparatus for 18 h to give [2-(isobutyryloxy)ethyl]-polystyrene. IR: 1733 cm^{-1} (C=O), 1155 cm^{-1} (ester C—O), no absorption characteristic of O—H str. Anal. Calcd for $(C_{10}H_{10})_{0.01}(C_8H_8)_{0.49}(C_{14}H_{18}O_2)_{0.50}$: C, 81.97; H, 8.13; Cl, 0. Found: C, 81.57; H, 8.20; Cl, 0.026.

[2-[[1-(Trimethylsiloxy)-2-methyl-1-propenyl]oxy]ethyl]polystyrene (4). To a solution of 5.6 mL (40 mmol) of diisopropylamine in 100 mL of THF at 0 °C was added 40 mmol of *n*-butyllithium (1.6 M in hexane). The solution was stirred 30 min at 0 °C, treated with 5 g of **3**, and stirred 2 h at 0 °C. The mixture was cooled to -78 °C, and 5.7 mL (45 mmol) of chlorotrimethylsilane was added. The mixture was stirred 1 h at -78 °C and 2 h at 0 °C. The product was isolated by filtration under argon, washed with THF, and extracted in a Soxhlet apparatus with sodium-dried THF to give 4.34 g of **4**. IR: 1702 cm^{-1} (silyl ketene acetal), 1730 cm^{-1} (ester C=O). Anal. Calcd for $(C_{10}H_{10})_{0.01}(C_8H_8)_{0.49}(C_{14}H_{18}O_2)_{0.04}(C_{17}H_{26}O_2Si)_{0.46}$: C, 76.50; H, 8.65; Si, 6.64. Found: C, 78.57; H, 8.01; Si, 6.61.

(Hydroxymethyl)polystyrene (6). To a suspension of 12 g of formylpolystyrene, $(C_{10}H_{10})_{0.01}(C_8H_8)_{0.84}(C_9H_8O)_{0.15}$, prepared by the procedure of Frechet and Hacque,[5] in 140 mL of

THF was added 0.3 g (32.6 mmol) of lithium aluminum hydride. After 12 h at reflux, the mixture was cooled and treated with 1 mL of water, 1 mL of 15% aqueous sodium hydroxide, and 3 mL of water. After 1 h, the mixture was filtered, and the filter cake was washed twice with 3 N hydrochloric acid, once with concentrated hydrochloric acid, three times with water, and twice with methanol. After drying there was obtained 12 g of (hydroxymethyl)polystyrene (**6**). IR: 3570 cm^{-1} (OH). No absorption attributable to C=O was detected. Anal. Calcd for $(C_{10}H_{10})_{0.01}(C_8H_8)_{0.84}(C_9H_{10}O)_{0.15}$: C, 90.10; H, 7.70. Found: C, 88.02; H, 7.80.

[(Isobutyryloxy)methyl]polystyrene. By use of essentially the same procedure as was used to prepare **3**, 6 g of **6** was converted to 6 g of [(isobutyryloxy)methyl]polystyrene. IR: 1735 cm^{-1} (ester C=O), 1150 cm^{-1} (ester C—O). Anal. Calcd for $(C_{10}H_{10})_{0.01}(C_8H_8)_{0.84}(C_{13}H_{16}O_2)_{0.15}$: C, 88.20; H, 7.78. Found: C, 87.58; H, 7.81.

[[[1-(Trimethylsiloxy)-2-methyl-1-propenyl]oxy]methyl]polystyrene (7). By use of essentially the same procedure as was used to prepare **4**, 6 g of [(isobutyryloxy)methyl]polystyrene was converted to 6.1 g of **7**. IR: 1705 cm^{-1} (silyl ketene acetal), 1735 cm^{-1} (ester C=O). Anal. Calcd for $(C_{10}H_{10})_{0.01}(C_8H_8)_{0.84}(C_{13}H_{16}O_2)_{0.05}(C_{16}H_{24}O_2Si)_{0.10}$: C, 86.02; H, 7.97; Si, 2.22. Found: C, 84.03; H, 7.93; Si, 2.25.

1-[2-[(3-Polystyryl-2,2-dimethylpropyl)oxy]ethoxy]-1-(trimethylsiloxy)-2-methyl-1-propene (9). A mixture of 10 g of (chloromethyl)polystyrene (1.36 mequiv/g), 1.25 g of anhydrous zinc chloride, 40 mL of dichloromethane, and 10.4 g of 1,2-bis[(1-trimethylsiloxy-2-methyl-1-propenyl)oxy]ethane[2b] was stirred at reflux under argon for 24 h. The product was isolated by filtration under an argon atmosphere and washed with dichloromethane and with THF. Extraction with THF gave 11.2 g of **9**. IR: 1705 cm^{-1} (silyl ketene acetal C=C), 1730 cm^{-1} (ester C=O), 1255, 845 cm^{-1} (Si—Me). Anal. Calcd for $(C_{10}H_{10})_{0.01}(C_8H_8)_{0.85}(C_9H_9Cl)_{0.04}(C_{22}H_{30}O_4Si)_{0.09}(C_{28}H_{34}O_4)_{0.01}$: C, 84.65; H, 7.69; Si, 1.87; Cl, 1.05. Found: C, 85.46; H, 8.03; Si, 1.86; Cl, 1.19.

Polymerization of MMA with 4. To a stirred mixture of 1 g of polystyrene-supported silyl ketene acetal $(C_{10}H_{10})_{0.01}(C_8H_8)_{0.49}(C_{14}H_{18}O_2)_{0.04}(C_{17}H_{26}O_2Si)_{0.46}$ (**4**) and 2.16 mL (20 mmol) of MMA in 15 mL of THF was added dropwise during 20 min 0.4 mL of tetrabutylammonium *m*-chlorobenzoate (0.1 M in THF). During this period the temperature of the reaction mixture rose 13 °C and then began to fall during the addition of the last of the catalyst solution. After 1 h, the reaction was quenched with 1 mL of methanol, and an aliquot of the supernatant was removed for NMR analysis, which showed no residual MMA. The product was collected by filtration. No polymer was recovered by evaporation of the filtrate. After extraction with THF in a Soxhlet apparatus for 18 h followed by drying in a vacuum oven, 2.93 g of graft copolymer **10** was obtained. IR: 1730 cm^{-1} (ester C=O). Anal. Calcd for $(C_{10}H_{10})(C_8H_8)_{49}(C_{14}H_{17}O_2)_{46}(C_5H_8O_2)_{389}$: C, 66.48; H, 8.00; Si, 0.0. Found: C, 66.08; H, 8.33; Si, 0.87.

Polymerization of MMA with 9. To a stirred mixture of 1 g of polystyrene-supported silyl ketene acetal $(C_{10}H_{10})_{0.01}(C_8H_8)_{0.85}(C_9H_9Cl)_{0.04}(C_{22}H_{30}O_4Si)_{0.09}(C_{28}H_{34}O_4)_{0.01}$ (**9**) and 15 mL of MMA was added dropwise 0.5 mL of tetrabutylammonium *m*-chlorobenzoate (0.1 M in THF) during 15 min. The temperature slowly rose 12 °C. After 3 h, the reaction mixture had solidified due to swelling of the polymer by MMA. After extraction with THF, 4.23 g of PMMA-grafted polystyrene was obtained.

Polymerization of MMA with 7. To a stirred mixture of 0.5 g of polystyrene-supported silyl ketene acetal $(C_{10}H_{10})_{0.01}(C_8H_8)_{0.84}(C_{13}H_{16}O_2)_{0.05}(C_{16}H_{24}O_2Si)_{0.10}$ (**7**) and 1.1 mL (10 mmol) of MMA in 8 mL of THF and 2 mL of acetonitrile was added 40 μL of tetrabutylammonium *m*-chlorobenzoate (0.38 M in THF). After 2 h, NMR analysis of the supernatant showed some residual MMA. The polymer was collected by filtration and extracted with THF in a Soxhlet apparatus to give 1.44 g (94% yield) of PMMA-grafted polystyrene. Anal. Calcd for $(C_{10}H_{10})(C_8H_8)_{84}(C_{13}H_{16}O_2)_{15}(C_5H_8O_2)_{310}$: C, 67.83; H, 7.98. Found: C, 67.75; H, 7.85. Evaporation of the supernatant gave 15 mg of PMMA ($M_n = 7580$, $M_w = 15\,900$, $M_w/M_n = 2.1$).

Polymerization of Acrylonitrile with 9. A stirred mixture of 0.66 mL of acrylonitrile, 10 mL of DMF, 2 mL of THF, and 1 g of $(C_{10}H_{10})_{0.01}(C_8H_8)_{0.85}(C_9H_9Cl)_{0.04}(C_{22}H_{30}O_4Si)_{0.09}(C_{28}H_{34}O_4)_{0.01}$ (**9**) was treated with 2 mL of $TASHF_2$ (0.01 M in DMF) dropwise during 30 min, which resulted in a modest increase in temperature initially. NMR analysis of the supernatant showed some residual monomer. The polymer was isolated by filtration and extracted with DMF. The combined filtrate and extract was concentrated in vacuo. Precipitation with water gave 0.14 g of poly(acrylonitrile). The insoluble copolymer was extracted with dimethyl sulfoxide and was then extracted in a Soxhlet apparatus with THF to give 1.19 g of graft copolymer. IR: 2240 cm^{-1} (CN), 1730 cm^{-1} (ester C=O). Anal. Calcd for $(C_{10}H_{10})_{0.01}(C_8H_8)_{0.85}(C_9H_9Cl)_{0.04}(C_{28}H_{34}O_4)_{0.01}(C_{18}H_{25}O_4[C_3H_3N]_8)_{0.09}$: C, 81.92; H, 7.29; N, 6.08. Found: C, 80.73; H, 7.81; N, 6.07. When the experiment was repeated at −50 °C, no soluble poly(acrylonitrile) was isolated, no residual monomer was detected by NMR, and 1.45 g of graft copolymer was isolated. IR: 2240 cm^{-1} (CN), 1730 cm^{-1} (ester C=O). Anal. Calcd for $(C_{10}H_{10})_{0.01}(C_8H_8)_{0.85}(C_9H_9Cl)_{0.04}(C_{28}H_{34}O_4)_{0.01}(C_{18}H_{25}O_4[C_3H_3N]_{12})_{0.09}$: C, 80.47; H, 7.13; N, 8.17; Cl, 0.77. Found: C, 78.94; H, 7.18; N, 8.32; Cl, 0.72.

Polymerization of Gaseous MMA and Acrylonitrile with 4. A mixture of 0.16 mL of tetrabutylammonium *m*-chlorobenzoate (0.38 M in THF) and 0.5 g of **4**, $(C_{10}H_{10})_{0.01}(C_8H_8)_{0.49}(C_{14}H_{18}O_2)_{0.04}(C_{17}H_{26}O_2Si)_{0.46}$, in 15 mL of THF was stirred for 30 min during which time **4** became yellow while the solution remained colorless. The polymer was isolated by filtration, dried (20 mTorr) and stored in a drybox. A 0.2-g sample of the polymer was placed in a shallow container in the drybox in close proximity to a shallow container containing 2 mL of MMA. After 24 h, the color of the polymer had lightened, and the weight had increased. After the polymer was dried at 20 mTorr 0.44 g of graft copolymer was obtained. IR: 1730 cm^{-1} (ester C=O). Extraction of 0.2 g of the product with THF for 3 days followed by evaporation of the filtered extract gave only 0.8 mg (0.4%) of solid. In a similar experiment with 50 mg of **4** and 1 mL of acrylonitrile, graft copolymer of styrene and acrylonitrile was obtained. IR: 2240 cm^{-1} (CN), 1735 cm^{-1} (ester C=O). Anal. Calcd for $(C_{10}H_{10})_{0.01}(C_8H_8)_{0.49}(C_{14}H_{18}O_2)_{0.50}(C_3H_3N)_{0.35}$: C, 80.52; H, 7.88; N, 2.72. Found: C, 80.29; H, 8.30; N, 2.71.

Chain Transfer in Polymerization of MMA in the Presence of 1. To a stirred mixture of 0.2 mL (1 mmol) of 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene, 1 g of **1**, $(C_{10}H_{10})_{0.01}(C_8H_8)_{0.49}(C_{10}H_9N)_{0.50}$, and 1 mL of MMA was added 30 μL of tetrabutylammonium *m*-chlorobenzoate (0.4 M in THF). Then a solution of 15 μL of tetrabutylammonium *m*-chlorobenzoate (0.4 M in THF) in 4.4 mL of MMA was added over 45 min. When the reaction temperature had returned to room temperature, a sample of the supernatant solution was removed for analysis. NMR analysis showed that of the MMA in solution, 8.5% was monomeric and 91.5% was PMMA. GPC: $M_n = 5240$, $M_w = 9070$, $M_w/M_n = 1.73$. The graft copolymer was removed by filtration, extracted with THF in a Soxhlet apparatus, and dried to give 2.6 of poly(styrene-*g*-MMA). IR: 1730 cm^{-1} (ester C=O), 2240 cm^{-1} (w, CN). From the combined filtrate and extracts 2.77 g of PMMA was isolated by precipitation with hexane.

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Registry No. (MMA)(styrene)(divinylbenzene (graft copolymer), 121876-32-2; (AN)(styrene)(divinylbenzene) (graft copolymer), 107939-65-1.

Synthesis and Characterization of Two Regiochemically Defined Poly(dialkylbithiophenes): A Comparative Study†

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ABSTRACT: The polymerization of 3,3′-dimethyl-2,2′-bithiophene and 3,3′-dihexyl-2,2′-bithiophene affords the stereoregular head-to-head versions of poly(3-methyl- and poly(3-hexylthiophene), respectively. The properties of the stereoregular polymers are compared to those of the conventional polymers obtained from polymerization of 3-methylthiophene and 3-hexylthiophene. Regiospecificity was determined via 500-MHz NMR (both ^{1}H and ^{13}C) in solution for the hexyl-substituted case and 300-MHz ^{13}C CPMAS for all polymers. The regiospecific polymers have their maximum absorption at considerably shorter wavelengths than their nonregiospecific counterparts; thus, poly(3,3′-dimethyl-2,2′-bithiophene) absorbs at a 91 nm shorter wavelength (417 vs 508 nm) and poly(3,3′-dihexyl-2,2′-bithiophene) absorbs at a 110 nm shorter wavelength (398 vs 508 nm). This change in band positions is not due to a difference in molecular weight since the two types of polymer are essentially of equal $\bar{M}_w$, with the stereoregular hexyl derivative having a slightly higher $\bar{M}_w$. We conclude that the intrachain sulfur–alkyl steric repulsion must be dominant, forcing the backbone out of coplanarity and π-conjugation. Interestingly, this pronounced steric effect on the electronic spectroscopy is not reflected in the conductivity. Finally, the stereoregular polymers are the most magnetic defect-free conjugated chains prepared to date, as determined via ESR spectroscopy.

Introduction

The isolation of amorphous solids from the reaction of thiophene with various catalysts dates back to 1883 with Victor Meyer's[1] "sulfuric acid wash" process for the purification of coal tar benzene in which thiophene was present as a contaminant. Since then, many reports on the polymerization of thiophene have appeared in the literature, but the products obtained were not well characterized and a structure was not determined.[2] Well characterized poly(thiophene) with a regular poly(2,5-thienylene) structure was obtained in 1979 by chemical polymerization[3] and later by electrochemical polymerization.[4] Since then, poly(thiophene) has been extensively studied and because of the ease with which the thiophene monomer can be 3-substituted, a large family of poly(thiophene) derivatives with remarkable properties has emerged.

Derivatives have been synthesized with the objective of obtaining a lower energy band gap and possibly intrinsically conducting polymers.[5] Polymerization of benzo[*c*]thiophene (isothianaphthene)[6] has produced the polymer, poly(isothianaphthene),[7] with the smallest band gap among the organic conducting polymers. Another polymer with an equally small band gap was more recently obtained from dithienothiophene.[7d] The decrease in the band gap when going from poly(thiophene) (2 eV) to poly(isothianaphthene) (1 eV) is explained[5] by an increase in the quinoid contribution to the electronic structure, caused by the fusion of the benzene to the thiophene ring. The same argument applies to poly(thieno[*c*]thiophene), which should also have a band gap of lower energy than poly(thiophene). Attempts to polymerize dihydrothieno[*c*]thiophene have been unsuccessful.[8]

Due to their rigid π-conjugated backbone and strong interchain interactions, all unsubstituted organic conducting polymers are insoluble and infusible. This constituted a major obstacle in their study and in the development of practical applications. An important step in the study of these materials occurred in 1983 with the preparation of solutions of organic conducting polymers in their doped form.[11] This was accomplished through a procedure in which the undoped polymer, suspended in AsF_3 solvent, was exposed to AsF_5 and doping occurred with concomitant dissolution. Films of the doped polymer could be cast by evaporation of the solvent. The process evolved to an in situ polymerization and doping, through dissolution of the monomer in liquid AsF_3/AsF_5. Solvation of the doped polymers in this system is attributed in large part to interactions between the inorganic dopant ions and the solvent. Two major drawbacks to this development are (1) the polymers cannot be redissolved after they have been cast into films and (2) the high toxicity of the AsF_3/AsF_5 system.

A major advance in the field of organic conducting polymers was the synthesis[12] of polymers that were soluble in common organic solvents in both their doped and

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