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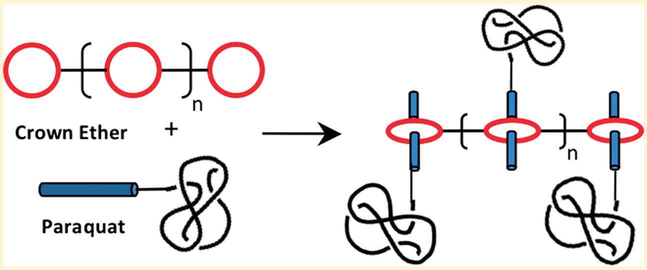
Supramolecular Pseudorotaxane Graft Copolymer from a Crown Ether Polyester and a Complementary Paraquat-Terminated Polystyrene Guest

Minjae Lee,[†] Robert B. Moore, and Harry W. Gibson*

Department of Chemistry, Virginia Polytechnic Institute & State University, Blacksburg, Virginia 24061-0212, United States

Supporting Information

ABSTRACT: The self-assembly of a polyester containing crown ether host repeat units and a paraquat-terminated polystyrene guest provides a supramolecular pseudorotaxane graft copolymer based on the bis(*m*-phenylene)-32-crown-10/paraquat recognition motif. NMR chemical shift changes in solution gave evidence of the complexation of the crown ether and paraquat moieties. Solutions of the two polymers at 1:1 host:guest stoichiometry (crown ether:paraquat), but only 3 mass % crown polymer, possessed an intrinsic viscosity 1.9 times that of the paraquat-terminated polystyrene and 2.7 times that of the polyester. Differential scanning calorimetry revealed only one glass transition for a solid from evaporation of a solution at 3:1 host:guest (crown ether:paraquat) stoichiometry; this indicated complete phase mixing, as confirmed by optical microscopy and small-angle laser light scattering.

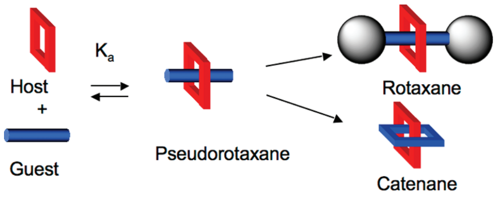


INTRODUCTION

In supramolecular chemistry, the formation of pseudorotaxanes, rotaxanes, and catenanes (Scheme 1) is a key subject, not only for better self-assembling systems but also for the expanded applications of noncovalent polymeric materials due to their unique topologies and hence properties.[1] The convergence of the two areas has led to construction of analogues of traditional covalently constructed polymeric structures and architectures by physically bound supramolecular methods. Linear,[2] dendritic,[3] star,[4,5] hyperbranched,[6] and metal-assisted[7] supramolecular pseudorotaxane polymers have been formed by self-organization of well-defined building blocks. Polymers containing terminal pseudorotaxane moieties were prepared by the introduction of host or guest moieties on the polymer chain ends via controlled polymerization techniques.[5,8,9] Polymer−polymer binding to form supramolecular pseudorotaxane-linked diblock copolymers was studied using these host- and guest-functionalized polymeric building blocks.[8,9]

Covalent comblike graft copolymers have been widely studied.[10−14] Three general methods for graft copolymer synthesis are "grafting from" reactions (formation of grafts from a polymer with pendant macroinitiator functionality), "grafting through" processes (homo- or co-polymerization of macromonomers containing a terminal polymerizable moiety), and "grafting onto" (attachment of preformed macromolecules to a polymer backbone).[11] Supramolecular graft copolymers of non-pseudorotaxane types have been reported by using hydrogen bonds between 2,7-diamido-1,8-naphthyridine (Napy) and 2-ureido-4[1*H*]-pyrimidinone (UPy) derivatives,[15] ionic interactions between carboxylate and pyridinium ions,[16] and terpyridine−ruthenium complexation.[17]

Scheme 1. Self-Assembly of Pseudorotaxanes from Cyclic Hosts and Linear Guests as Precursors of Rotaxanes and Catenanes[a]



[a] The red squares refer to cyclic host moieties. The blue rods represent guest species. The black filled balls in the rotaxane portray blocking groups or stoppers. The blue square in the catenane is the cyclic species formed from the linear guest.

Graft copolymers based on pseudorotaxane or rotaxane linkages appear to offer some unique properties. There are two types of grafting situations: (1) the graft emanates from a pseudorotaxane or rotaxane unit that is part of the backbone, and (2) the graft is attached via a pendant pseudorotaxane or rotaxane moiety. Main chain systems (type 1) are depticted in Scheme 2. Structure **A** represents a pseudorotaxane built from a

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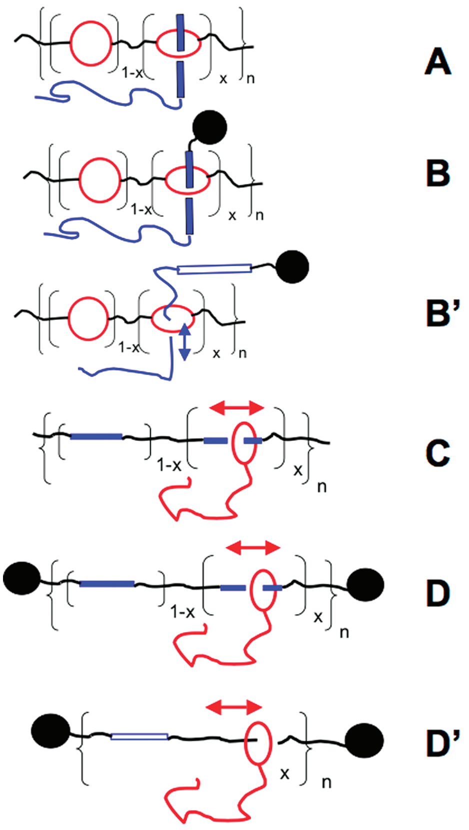
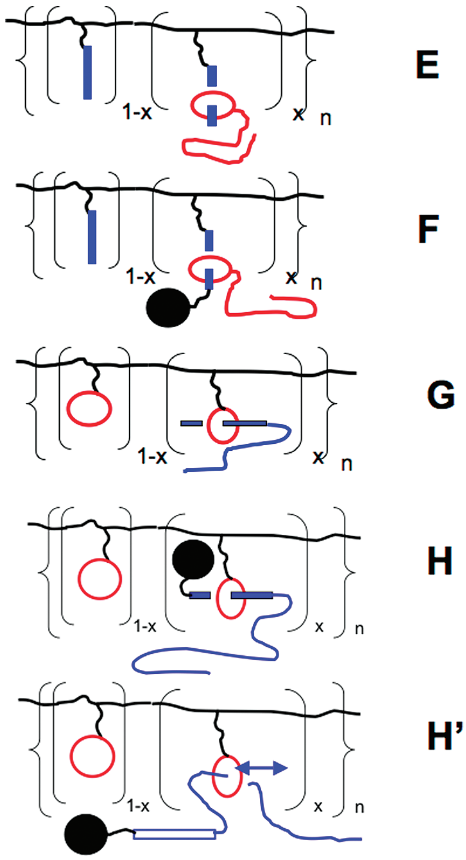
Scheme 2. Cartoon Representations of "Main Chain" Pseudorotaxane Graft Copolymers[a]



[a] **A** and **B** result from polymers with host macrocycles in the backbone. **C** and **D** are formed from polymers with guest species in the backbone. The red circles and ellipses refer to cyclic host moieties. The black filled circles portray blocking groups or stoppers. The filled blue rectangles represent active guest species, while the empty blue rectangles in **B**′ and **D**′ correspond to deactivated guests. The double headed arrows indicate possible movement of the cyclic or linear component relative to the other.

polymacrocycle, and **B** is the corresponding rotaxane derived therefrom. Cartoon **C** portrays a pseudorotaxane with a host-terminated polymer bound to a guest-containing main chain, and **D** is the rotaxane analogue. Likewise, side chain graft pseudorotaxanes (type 2) are shown in cartoon form in Scheme 3; **E** and **F** correspond to grafts formed via a polymer with pendant guest moieties, while **G** and **H** represent pseudorotaxanes and rotaxanes from polymers bearing host pendants. Pseudorotaxane systems possess inherent reversibility and response to external stimuli, such as pH, solvent, temperature, redox events, chemical reactions, etc.,[1] and therefore could be turned on or off by these means. On the other hand, true rotaxane linkages are expected to endow the graft copolymer with permanence but allow motion of the grafted chains relative to the main chain, unlike covalent graft copolymers. In the rotaxanes deactivation of the active guest sites by one of these stimuli should allow the threaded polymer to slide through the cyclic host in response to external forces such as shear, surface energetics, solvation, etc. These responses would be unique to the rotaxane grafts relative to covalent analogues whose components are fixed to each other at one point in a very specific manner. Examples of such responsive rotaxane systems are illustrated in cartoon form as **B**′ and **D**′ in Scheme 2 and **H**′ in Scheme 3.

Scheme 3. Cartoon Representations of "Pendant Group" Pseudorotaxane Graft Copolymers[a]



[a] **E** and **F** are derived from polymers with pendant guest moieties. **G** and **H** can be prepared from polymers with pendant host units. The red circles and ellipses refer to cyclic host moieties. The black filled circles portray blocking groups or stoppers. The filled blue rectangles represent active guest species, while the empty blue rectangle in **H**′ corresponds to a deactivated guest. The double-headed arrows indicate possible movement of the cyclic or linear component relative to the other.

It is noteworthy in this respect that in earlier work we have prepared precursors to many of these graft pseudorotaxanes. Poly(ester rotaxane)s,[18] poly(amide rotaxane)s,[19] and poly(urethane rotaxane)s[20] based on crown ethers have been synthesized and studied. Several aspects of these systems are relevant to the present topic. The polyester rotaxanes result from hydrogen bonding of the diol monomers with crown ethers during synthesis, but in the polymers themselves there is little attractive interaction between the macrocycle and the backbone; this allows rather free motion of the threaded cyclic species along the main chain as deduced from the fact that the macrocycles can aggregate and crystallize;[18c,e,21] translated to the graft copolymers of structures **B**′, **D**′ (Scheme 2), and **H**′ (Scheme 3) this mobility should result in good response to solvent and interfacial effects. On the other hand, the poly(urethane rotaxane)s display fairly strong interaction between the urethane moieties and the crown ethers in nonpolar media[20e,f] or the solid state;[20d] however, the loci of the macrocycles can be changed by exposure to polar solvents as we demonstrated.[20e,f] A further useful feature based on the attractive interaction is that preformed polyurethanes can be threaded by crown ethers simply by mixing the two components,[20h] enabling facile preparation of polypseudorotaxanes with varied cyclic components, including initiator functionalized and polymeric species. The very slow dethreading (half-life ~1 year) observed with the polyester rotaxanes[18f] demonstrates that due to the random coiling of flexible macromolecules blocking groups or stoppers may not be necessary for threaded polymers with even modest molecular weights. We have also prepared polymethacrylates with pendant crown ether moieties suitable for grafting via pseudorotaxanes as demonstrated by model studies.[22] And as noted above, we have synthesized narrow polydispersity polymers bearing crown ether terminal groups[5,8,9] and dialkylammonium[5] and paraquat[9] terminal groups as well.

Cyclodextrin-based polyrotaxanes have been utilized to prepare rotaxane graft copolymers[23] using the "graft onto" approach utilizing either the hydroxyl groups on the macrocycle[23a−d] or via copper-catalyzed alkyne−azide cycloaddition chemistry.[23e] In these systems the linkage to the backbone is a rotaxane moiety, enabling the grafted chain to move along the main chain's backbone (Scheme 2, structure **D**).

However, to our knowledge, no examples of any of the pseudorotaxane or rotaxane types of supramolecular graft copolymers shown in Schemes 2 and 3 based on crown ethers or cryptands have been reported to date. Here we report the preparation of a supramolecular comblike graft copolymer based on crown ether-based pseudorotaxane formation in a manner analogous to the "grafting onto" approach, i.e., structure **A** (Scheme 2). A specific aim was to determine whether, in analogy to covalent graft copolymers, formation of such a pseudorotaxane graft copolymer would result in compatibilization of two otherwise incomplatible polymers.

EXPERIMENTAL SECTION

Materials. The poly(ester crown ether) **1** (M_n = 28.5 kDa) was synthesized previously.[18j] The paraquat-terminated polystyrene **2** (M_n = 31.5 kDa and PDI = 1.07) was also previously synthesized[9] and characterized by ^{1}H NMR and high resolution electrospray ionization time-of-flight mass spectrometry (HR ESI TOF MS). The nonfunctionalized polystyrene (M_n = 60.0 kDa, PDI = 1.15) was synthesized by atom transfer radical polymerization.[24] All the solvents were HPLC grade and used as received.

Instruments. Gel permeation chromatography (GPC) was conducted on an ISCO model 2350 chromatograph equipped with a light scattering detector (miniDAWN, 690 nm) and a generic refractive index detector at 23 °C using dual Polymer Laboratories columns (PLgel mixed 5 μm × 300 mm) packed with cross-linked styrene−divinylbenzene; the solvent was THF. The system was calibrated with polystyrene standards with molecular weights between 1.25 and 100 kDa/mol. ^{1}H NMR spectra were obtained on Varian Unity and Inova 400 MHz NMR spectrometers. DSC results were obtained on a TA Instruments Q2000 differential scanning calorimeter at a scan rate of 5 °C/min heating under N_2 purge; only results of second scans are reported. HR ESI TOF MS was carried out on an Agilent 6220 Accurate Mass TOF LC/MS spectrometer in positive ion mode. The morphology in thin film samples (between glass coverslips) was investigated by optical microscopy in phase contrast mode under variable temperature conditions using a Nikon LV100 microscope equipped with a Nikon DXM1200 digital camera. Thermal control of the samples was achieved using a Linkam THMS600 hot stage paired with a Linkam TMS 94 system controller. All micrographs were collected using Nikon NIS-Elements software. Small-angle laser light scattering (SALLS) was conducted on thin film (ca. 10 μm thick) samples cast from chloroform solution onto glass microscope slides. The SALLS system consisted of an Oriel He−Ne laser (633 nm wavelength) and a Photometrics SenSys 1401E CCD detector. SALLS patterns were collected in V_v mode with a sample to image plane distance of 318 mm using RS Image software and processed using WinView32 and MDI Polar software.

RESULTS AND DISCUSSION

The self-assembly of a polyester host containing crown ether units in its main chain and a paraquat-terminated polystyrene guest provides a new supramolecular graft copolymer based on the well-known bis(*m*-phenylene)-32-crown-10/paraquat recognition motif for pseudorotaxane formation.[1,2a,2f,2g,4a,6a,7b,9,18j,18k,20c,25−30]

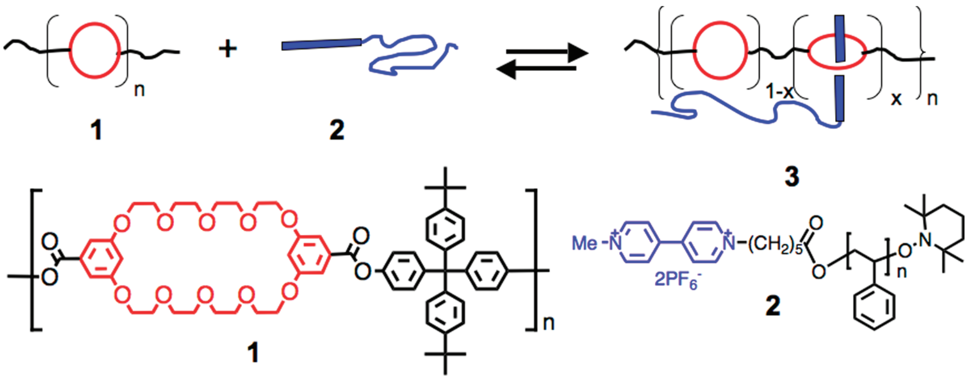
The main-chain crown polyester host **1**[18i] (Scheme 4) was used as the backbone of the comblike graft copolymer. The molecular weight of **1** was determined by GPC: M_n = 28.5 kDa.[18i] The average degree of polymerization was 27; on average, 27 grafting sites are available on the each polyester chain. The paraquat (*N,N*′-dialkyl-4,4′-bipyridinium salt)-terminated polystyrene **2** was prepared by nitroxide mediated polymerization (NMP) as previously reported.[9] The paraquat end-functionality was confirmed by ^{1}H NMR and ESI TOF mass spectrometry (see Supporting Information). The molecular weight and polydispersity of **2** were analyzed by GPC: M_n = 31.5 kDa and PDI = 1.07.

The graft copolymer **3** was formed in solution (Scheme 4) as an example of structure **A** of Scheme 2. The best solvent we found was chloroform, which dissolves both starting polymers **1** and **2**; furthermore, it is rather nonpolar so it will not inhibit crown ether−paraquat complexation. The stoichiometry of **1** and **2** can be varied. However, due to the fact that the paraquat polymer **2** is of significant molecular weight and occupies significant volume, full occupancy of the crown ether sites on the polyester will most likely not be achieved as a result of both electrostatic and steric repulsions.

The first evidence for the formation of the graft copolymer **3** came from NMR studies. The chemical shift changes of the crown ether protons of **1** and the paraquat protons of **2** in the ^{1}H NMR spectrum (Figure 1) clearly indicate complexation of these units in solution. The chemical shift changes and the fast-exchange nature of the complexation process are analogous to those observed in the binding between the corresponding small molecule hosts and guests, bis(*m*-phenylene)-32-crown-10 and derivatives with paraquats.[1,25−30] The ethyleneoxy protons of uncomplexed **1** appear at δ 4.18, 3.86, 3.72, and 3.69. However, the first two peaks shifted to δ 4.10 and 3.83, and the last two peaks merged upon addition of paraquat-terminated polystyrene **2** (crown ether:paraquat = 1:1 mol/mol). NMR does not easily afford a quantitative estimate of the association constant between two polymeric species because the maximum chemical shift change (Δ_0) required to analyze this fast-exchange system is difficult to measure.[31]

The formation of a graft copolymeric pseudorotaxane was confirmed by viscosity studies as shown in Figure 2. Solutions of crown polyester **1** and paraquat polystyrene **2** [**1**:**2** = 1:27 mol:mol (from GPC M_n values), crown ether:paraquat = 1 mol:1 mol] possessed an "intrinsic viscosity" ([η] = 0.519 dL g^{-1}) nearly double that of paraquat-teminated polystyrene **2** ([η] = 0.269 dL g^{-1}) and nearly triple that of polyester **1** ([η] = 0.183 dL g^{-1}), consistent with the formation of the comblike graft

Scheme 4. Schematic Illustration of the Formation of a Supramolecular Graft Copolymer 3 from Poly(ester crown ether) 1 and Paraquat-Terminated Polystyrene Guest 2 in Solution



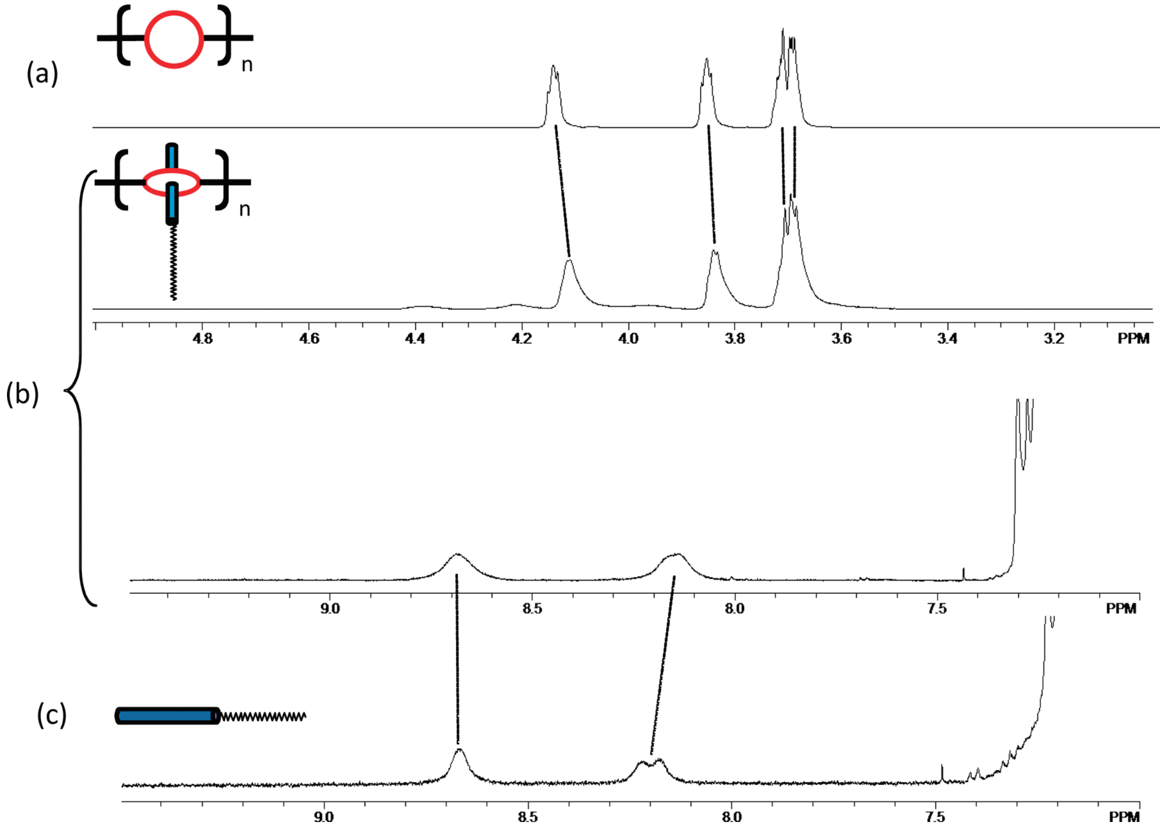


Figure 1. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, 23 °C) of (a) poly(ester crown ether) **1**, (b) polyester **1** and paraquat-terminated polystyrene **2** (mass ratio **1**:**2** = 1.0:16; ratio of crown ether moieties to paraquat moieties = 1.8:1.0, concentration of **2** = 5.0 mM), and (c) paraquat-terminated polystyrene **2**.

copolymer. Note that this value is not a true intrinsic viscosity because the extent of complexation, i.e., x in **3** (Scheme 4), decreases with decreasing concentration. Nonetheless, the increase in viscosity is quite remarkable, given that the samples contained only 3.2 wt % of polyester **1**!

The DSC results corroborate the formation of graft copolymer **3** and compatibilization of the two substantially different polymers. The DSC heating traces of **1**, **2**, an uncomplexed solid mixture of **1** and **2**, and copolymer **3** are shown in Figure 3. The T_g of the crown polyester **1** is 109.3 °C, and the T_g of the paraquat polystyrene **2** is 103.4 °C. The uncomplexed solid mixture of the two components exhibits two T_gs that exactly correspond to the T_gs of the components. However, the self-assembled graft copolymer **3** has only one T_g (98.6 °C), and it is lower than both **1** and **2**, reflective of an increase in free volume as result of the grafting process and the presence of a single phase in the dual component blend. Simple mixing of **1** and **2** in solution led to the formation of the graft copolymer **3**, but mixing the polymers in the solid state did not. The DSC result from the immiscible blend of **1** and nonfunctionalized polystyrene

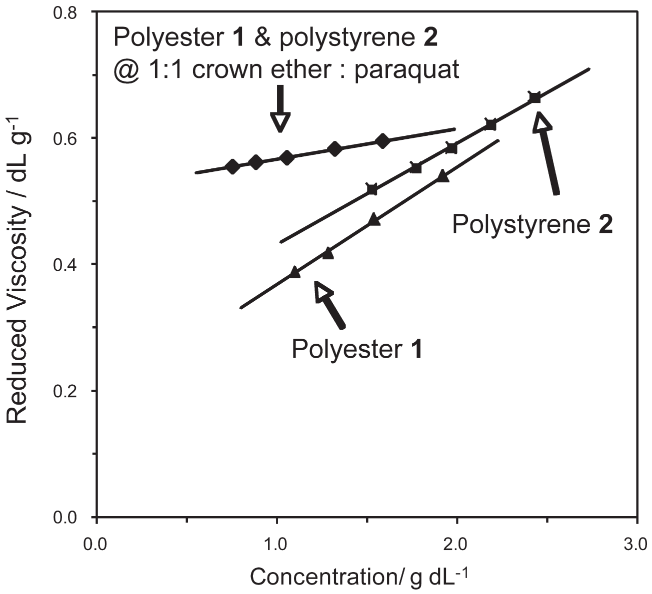


Figure 2. Reduced viscosity as a function of concentration (chloroform at 25 °C): (a) crown polyester **1**: $y = 0.183 + 0.186x$, $r^2 = 0.999$; (b) paraquat-terminated polystyrene **2**: $y = 0.269 + 0.162x$, $r^2 = 0.998$; and (c) **1** and **2** (mass ratio **1**:**2** = 1.00:29.8; ratio of crown ether to paraquat moieties = 1.00:1.00): $y = 0.519 + 0.0481x$, $r^2 = 0.999$.

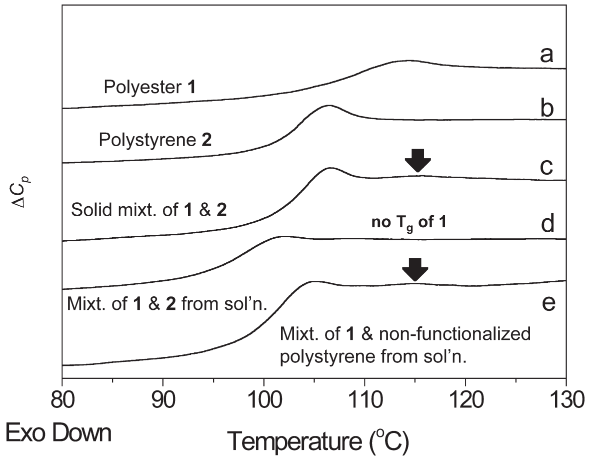


Figure 3. DSC traces of (a) poly(ester crown ether) **1**, (b) paraquat-terminated polystyrene **2**, (c) solid mixture of **1** and **2**, (d) blend from a solution (chloroform) of **1** and **2**, and (e) blend from a solution (chloroform) of **1** and the nonfunctionalized polystyrene (M_n 60.0 kDa). All the traces are from the second heating scans. The ratio of crown ether to paraquat moieties was 3.0:1.0 for (c) and (d) (mass ratio **1**:**2** = 1.00:9.95). For (e) the mass ratio of **1**:PS was 1.00:9.95.

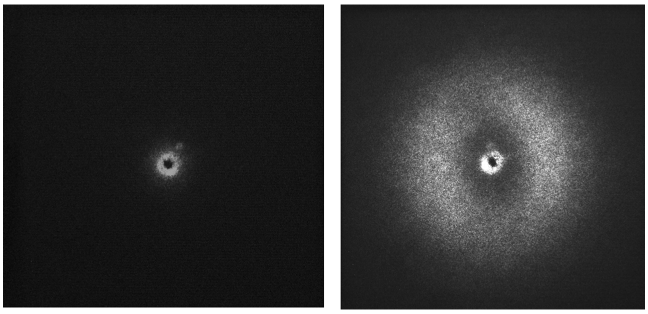


Figure 4. SALLS images of a solution (chloroform) cast mixture of poly(ester crown ether) **1** and polystyryl paraquat **2** (left) at 3.0:1.0 molar ratio of crown ether:paraquat moieties (mass ratio **1**:**2** = 1.00:9.95) and a solution (chloroform) cast mixture of polymer **1** and polystyrene (M_n 60.0 kDa) with no functional group (at 1.00:9.95 mass ratio of **1**:PS, right).

(M_n = 60.0 kDa, PDI = 1.15, T_g = 102.0 °C) substantiated this conclusion; the solution blend of **1** and the nonfunctionalized polystyrene led to a mixture with two T_gs because macroscopic phase separation occurred without the paraquat functionality on the polystyrene, i.e., the ability to form the pseudorotaxane graft copolymer. The complete miscibility of **1** and **2** is explained by the supramolecular complexation of the two polymers to form graft copolymeric pseudorotaxane **3**. Thus, although perhaps not all of the paraquat-terminated polystyrene was complexed, the grafted polystyryl arms compatibilized any uncomplexed macromolecules **2** with the polyester, just as is the case with covalent graft copolymers as compatibilizers for the two respective linear components.[32,33]

Optical microscopy and small-angle laser light scattering (SALLS) analysis reinforce the DSC experiments. As expected, a film of the graft copolymeric pseudorotaxane **3** (crown ether: paraquat = 3.0:1.0) did not display macroscopic phase separation by either optical microscopy or SALLS (Figure 4). However, the blend of polyester **1** and the nonfunctionalized polystyrene revealed a distinct scattering halo that is characteristic of typical macroscopic phase separation in polymer blends.[32] Macrophase separation of the blend from **1** and **2** does not take place because of the complexation of the two species to form graft copolymer **3**. Even though this result does not indicate the complete formation of the pseudorotaxane, i.e., the extent of grafting, this new supramolecular method clearly results in compatibilization of otherwise incompatible polymers, polystyrene, and the poly(ester crown ether).

■ CONCLUSIONS

We have reported the first supramolecular comblike graft copolymer **3** based on pseudorotaxane formation from two polymeric building blocks: a main-chain crown ether polyester **1** and a paraquat-terminated polystyrene **2**. The formation of the graft copolymer **3** was proven by NMR chemical shift changes in solution, a dramatic viscosity increase in solutions of the two components, the observation of a single T_g by DSC, and the lack of phase separation by both optical microscopy and SALLS. Introduction of appropriate blocking groups onto the paraquat units of this system after complexation will produce a mechanically interlocked comblike graft copolymeric rotaxane (structure **B** of Scheme 2). We provided one example of a pseudorotaxane supramolecular graft copolymer, and we are investigating other polymeric architectures constructed using such supramolecular approaches.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. ^{1}H NMR spectrum, ESI TOF MS spectrum of polymer **2**, and optical microscopic images of mixtures of the polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail hwgibson@vt.edu; Fax 540-231-8517; Tel 540-231-5902.

Present Addresses

†Samsung Total Petrochemicals, Co. Ltd., Seosan-si, Korea.

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(31) For fast exchange host−guest systems in proton NMR, only time-averaged peaks appear, as with our current system. In this case, the maximum chemical shift change (Δ_0) is required to calculate K_a. Usually Δ_0 is measured by keeping the concentration of one component constant and increasing that of the other to very high values; Δ_0 is the zero intercept in a plot of the chemical shift change versus the inverse of the concentration of the variable component (Tsukube, H.; Furita, H.; Odani, A.; Takeda, Y.; Kudo, Y.; Inoue, Y.; Liu, Y.; Sakamoto, H.; Kimura, K. In *Comprensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vögtle, F., Eds.; Pergamon: New York, Vol. 8, Chapter 10, pp 425−482). However, in the present system with polymeric host and guest the concentrations that can be applied are limited because the resulting high viscosity broadens the peaks so as to preclude accurate chemical shift measurements.

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