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Fluorinated Amphiphilic Block Copolymers: Combining Anionic Polymerization and Selective Polymer Modification

Marc A. Hillmyer,[1] Nathan W. Schmuhl,[2] Timothy P. Lodge*[1,2]*

[1]Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, USA
E-mail: hillmyer@chem.umn.edu; lodge@chem.umn.edu
[2]Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, USA

Summary: We report the preparation of novel fluorinated block copolymers using a two-step modification sequence. We first prepared model polyisoprene-poly-*tert*-butylmethacrylate block copolymers by anionic polymerization. Exposing these materials to difluorocarbene (generated by the thermolysis of hexafluoropropylene oxide) resulted in modification of the polyisoprene block to the corresponding difluorocyclopropane repeating unit without compromising the integrity of the poly-*tert*-butylmethacrylate block. Hydrolysis of the difluorocarbene-modified materials gave the corresponding difluorocarbene-modified polyisoprene-polymethacrylic acid diblock copolymers. These amphiphilic materials are expected to exhibit interesting self-assembly behavior in aqueous solution.

Keywords: anionic polymerization; block copolymers; fluoropolymers; modification; self-assembly

Introduction

The preparation of block copolymers containing a fluorinated block can be accomplished using a variety of synthetic strategies. These include sequential addition of monomers using a controlled/living polymerization scheme,[1] coupling of an end-functionalized fluorinated polymer with another end-functionalized material, and selective post-polymerization fluorination[2] of one segment of a parent block copolymer. Although all these methods have advantages, the last approach is particularly useful since, in principle, the level of fluorination can be controlled using either reaction time or stoichiometry. This allows for the systematic incorporation of fluorine, thereby generating block copolymer materials with tunable properties. The unique properties of fluorinated polymers motivate the preparation of such hybrid materials. Biocompatibility, low surface energy, unique solubility characteristics, and general incompatibility with most other polymers are a subset of the distinctive features of fluoropolymers that make their study particularly interesting. The combination of fluoropolymers with water-soluble macromolecules in one hybrid material (i.e., a block copolymer) yields "highly amphiphilic" materials that can

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self-assemble in aqueous solution to give micellar structures at very low concentration (i.e., very low critical micelle concentrations) and can be used as dispersants, drug delivery vehicles, or viscosity modifiers. The preparation of such amphiphilic materials is described in this paper. We have taken a synthetic approach that involves the preparation of well-defined polyisoprene-poly-*tert*-butylmethacrylate diblock copolymers by sequential anionic polymerization.[3] Using a polydiene modification scheme that incorporates difluorocarbene in the polyisoprene backbone,[4] we have prepared the difluorocarbene-modified variants without significant degradation. Hydrolysis of the resultant fluorinated block copolymers gives the final amphiphilic materials. This work demonstrates that poly-*tert*-butylmethacrylate blocks are inert under the reaction conditions used for the difluorocarbene addition to polyisoprene, and that the hydrolysis of the poly-*tert*-butylmethacrylate segments can be accomplished without compromising the structural integrity of the difluorocyclopropane repeat unit in the difluorocarbene-modified polyisoprene block. The modification procedure is shown in Figure 1.

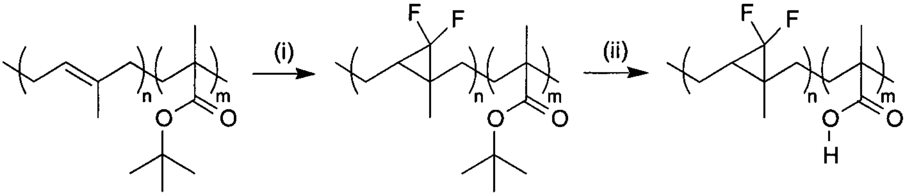

Figure 1. Sequential modification of polyisoprene-poly-*tert*-butylmethacrylate block copolymers. (i) Hexafluoropropylene oxide, 180 °C. (ii) Methanesulfonic acid / acetic acid, 100 °C.

Polyisoprene-poly-*tert*-butylmethacrylate block copolymers

The general synthetic protocol for the polyisoprene-poly-*tert*-butyl methacrylate (PI-PtBMA) diblock copolymers is as follows. The PI blocks were synthesized in cylcohexane (to obtain the desired 4,1 microstructure) at 40 °C using *s*ec-butyl lithium as the initiator. A typical concentration of the polyisoprenyllithium chain ends was approximately 5 $\text{mmol}\cdot\text{L}^{-1}$. After allowing 4 h for isoprene polymerization, an equal volume solution of LiCl predissolved in THF (typically having a concentration of 1.5 g of LiCl per liter of THF) was added to the reaction. As the THF solution was added, the temperature was slowly reduced to near −78 °C. The solution turned lemon yellow, indicating living polyisoprenyl anions in a polar solution. Once all of the THF solution was added and the reaction temperature was below −70 °C, the *tert*-butyl methacrylate was added. This resulted in a colorless solution, which was allowed to react for an additional 4 h. Termination was carried out by the addition of degassed methanol at the reaction temperature. Higher molecular weight PI-PtBMA polymers and those with large percentages of PtBMA were precipitated in deionized water. Precipitation in water removed some of the salt added in the reaction. The lower molecular weight polymers with a higher fraction of PI were concentrated, re-dissolved in hexane and filtered. The resulting solutions were again concentrated, diluted with THF and cast to dry.[5]

Table 1 summarizes the molecular characteristics for the PI-PtBMA block copolymers. The PI volume fractions (f_{PI}) were calculated using densities of PI = 0.91[3] and PtBMA = 1.022[6] g·cm^{-3} at 25 °C and the molar ratios from ^{1}H-NMR spectra. The molecular weights for these polymers were determined by SEC, both in comparison to polystyrene standards and using multi-angle light scattering (MALS) detection. The polydispersity indices (M_w/M_n) for the PI-PtBMA block copolymers were based on SEC using polystyrene standards. In all cases, polydispersities were less than 1.1.

Table 1. Molecular characteristics PI-PtBMA diblock copolymers.

Sample code	f_{PI}	M_n (kg·mol^{-1})^a	M_n (kg·mol^{-1})^b	M_n (kg·mol^{-1})^c	M_w/M_n^{c}
PI-PtBMA 9-2	0.74	10	10	29	1.04
PI-PtBMA 7-4	0.51	11	11	27	1.04
PI-PtBMA 4-7	0.25	11	10	28	1.05
PI-PtBMA 26-4	0.77	31	30	55	1.07
PI-PtBMA 22-10	0.55	32	29	59	1.03
PI-PtBMA 12-20	0.25	32	31	66	1.05

(a) Calculated based on quantitative monomer conversion and reaction stoichiometry.
(b) Determined by SEC with MALS detector using dn/dc calculated from dn/dc_{PI} = 0.124 and dn/dc_{PtBMA} = 0.079 mL·g^{-1} in THF.
(c) Determined by SEC with polystyrene standards.

Fluorination of PI-PtBMA Block Copolymers with Difluorocarbene

Cyclohexane solutions of the PI-PtBMA block copolymers were subjected to hexafluoropropylene oxide (HFPO) at 180 °C using a high-pressure reactor.[4] The thermolysis of HFPO generates difluorocarbene[7] and this adds selectively to the double bonds in the PI backbone. Prolonged reaction times were avoided since the PtBMA was somewhat sensitive to degradation at long reaction times. Additionally, 5 wt% 2,6-di-tert-butyl-4-methylphenol (BHT), a radical scavenger, relative to the weight of the PI block was also added to the mixture to prevent crosslinking. Reaction times necessary for complete conversion of the PI double bonds were determined in a separate study.[8] After the reaction the polymer solution was filtered, concentrated to dryness, redissolved in THF, and reverse precipitated in a 10:1 mixture of water/methanol. The precipitated polymer was collected and dried first at room temperature and then at 100 °C under vacuum < 100 mTorr for 48 h.

Using a combination of ^1H and ^{19}F NMR spectroscopies we determined that the PI block was selectively CF_2-modified to give FPI-PtBMA. The molecular characteristics of the difluorocarbene-modified FPI-PtBMA diblock copolymers are summarized in Table 2.[9] Molecular weights and FPI volume fractions (f_{FPI}) were calculated using the precursor PI-PtBMA molecular weights, assuming no degradation or side-reactions, and using RT densities (FPI = 1.26[10] and PtBMA = 1.022[6] $g \cdot cm^{-3}$). Molecular weights were also determined with SEC using polystyrene standards and MALS and molecular weight distributions were calculated using polystyrene standards. Percent conversions of the polyisoprene double bonds were measured from the ^1H NMR spectra of the FPI-PtBMA block copolymers, and in all cases the conversions were > 99%.

These results presented in Table 2 are noteworthy since they are the first reported examples of the successful use of difluorocarbene for the modification of polydienes in the presence of methacrylates; the analogous difluorocarbene modification of polydienes in the presence of polystyrene blocks has been documented previously.[10] All polymers retained their narrow molecular weight distributions after CF_2 modification, with good agreement between the predicted molecular weights and those determined by using SEC/MALS. ^1H NMR spectra for these polymers indicated complete conversion of the PI blocks to FPI with little to no degradation of the PtBMA blocks. The volume fractions of the PtBMA blocks are significantly lower after fluorination due to the significant increase in the molecular weight of the FPI block from the addition of the two fluorine atoms and one carbon atom to each repeat unit.

Table 2. Molecular characteristics of the FPI-PtBMA diblock copolymers.

Sample code	f_{FPI}	M_n ($kg \cdot mol^{-1}$)^a	M_n ($kg \cdot mol^{-1}$)^b	M_w/M_n^{b}	Precursor
FPI-PtBMA 15-2	0.93	17	25	1.06	PI-PtBMA 9-2
FPI-PtBMA 12-4	0.83	19	30	1.06	PI-PtBMA 7-4
FPI-PtBMA 7-7	0.62	16	21	1.05	PI-PtBMA 4-7
FPI-PtBMA 46-4	0.94	47	58	1.07	PI-PtBMA 26-4
FPI-PtBMA 38-10	0.85	47	94	1.06	PI-PtBMA 22-10

(a) Determined by SEC with MALS detection using dn/dc calculated with $dn/dc_{FPI} = 0.04$ and $dn/dc_{PtBMA} = 0.079\ mL \cdot g^{-1}$ in THF.

(b) Determined by SEC with polystyrene standards.

Hydrolysis of the FPI-PtBMA Block Copolymers

Hydrolysis reactions were performed in toluene using methanesulfonic acid (MSA) and acetic acid (AA) in the presence of BHT at 100 °C for 6h.[11] After the reaction, the solution was cooled to RT, concentrated to dryness, redissolved in THF, and precipitated in a 10:1 mixture of water/methanol. The precipitated polymer was collected, washed thoroughly with water, and dried first at room temperature under argon and then at 100 °C under reduced pressure (< 100 mTorr) for 48 h.

The results for the conversion of FPI-PtBMA to the corresponding polymethacrylic acid block copolymers (FPI-PMAA) are given in Table 3. While dramatic discrepancies were seen between predicted and measured M_n values for the FPI-PMAA 15-1 and 12-2 samples, FPI-PMAA 46-3 and 38-6 both exhibited M_n values fairly close to the predicted values based on complete conversion and no degradation. One possible reason for the discrepancy in the predicted and measured molecular weights for the FPI-PMAA 15-1 and 12-2 samples is some aggregation of the these materials in THF given their higher PMAA contents. However, the relatively narrow molecular weight distributions of these materials is not entirely consistent. Generally, molecular weight distributions were not observed to increase dramatically, except in the case of FPI-PMAA 12-2.

Table 3. Molecular characteristics of FPI-PMAA diblock copolymers.

Sample code	M_n ($kg{\cdot}mol^{-1}$)^a	M_n ($kg{\cdot}mol^{-1}$)^b	M_n ($kg{\cdot}mol^{-1}$)^c	M_w/M_n^{c}	Precursor
FPI-PMAA 15-1	16	80	53	1.04	FPI-PtBMA 15-2
FPI-PMAA 12-2	14	160	20	1.28	FPI-PtBMA 12-4
FPI-PMAA 46-3	49	48	57	1.07	FPI-PtBMA 46-4
FPI-PMAA 38-6	44	52	96	1.11	FPI-PtBMA 38-10

(a) Calculated value assuming 100% conversion and no FPI degradation or side reactions.

(b) Determined by SEC with MALS detector using dn/dc calculated with dn/dc_{FPI} = 0.04 and dn/dc_{PMAA} = 0.084 $mL{\cdot}g^{-1}$ in THF.

(c) Determined by SEC with polystyrene standards.

Conclusion

We have shown that model PI-PtBMA block copolymers prepared by sequential anionic polymerization can be selectively modified first by addition of difluorocarbene to the PI block and second by hydrolysis of the *tert*-butyl ester moieties in the PtBMA block. The self-assembly of these molecules in aqueous solution will be explored. These block copolymers have the potential to form interesting structures in water based on the high incompatibility of the fluorinated and water-soluble blocks.[12]

Acknowledgement

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