RAFT polymerization of fatty acid containing monomers: controlled synthesis of polymers from renewable resources†

Binoy Maiti and Priyadarsi De*

The incorporation of bio-renewable resources such as fatty acids into the polymer chain allows tailoring the properties of products, for their widespread applications. A series of methacylate monomers with side-chain fatty acids (FAMA) were synthesized by esterification of 2-hydroxyethyl methacrylate (HEMA) and fatty acids, such as caprylic, capric, lauric, myristic, palmitic and stearic acid. Consequent polymerization of FAMAs via reversible addition-fragmentation chain transfer (RAFT) gave side-chain fatty acid-containing well-defined polymers (PFAMA) with targeted molecular weights, narrow molecular weight distribution and precise chain-end functionality. The PFAMAs were subsequently used as macro-chain transfer agents (macro-CTA) for the polymerization of 2-(2-methoxyethoxy)ethyl methacrylate (MEO2MA) to obtain block copolymers. Homopolymers with fatty acid pendants display crystalline behaviour depending on the chain length of the fatty acids, evidenced by differential scanning calorimetry (DSC), polarized optical microscopy, small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) techniques.

Introduction

The use of renewable resources in various applications is receiving growing attention from both industry and academia. Fatty acids (FA) and their derivatives are important bio-renewable resources, they are readily available, inexpensive, biocompatible and find numerous applications in diverse fields. Fatty acid derivatives have been used in the area of macromolecular science for a long period of time for the synthesis of varieties of monomers as well as linear and cross-linked polymers of different types (e.g. polylefins, polyesters, polyethers, polyamides, epoxy and polyurethane resins, and others) via step-growth polymerization mechanism. Recent progresses on the preparation of vegetable oil-based thermoplastic polyesters and polyurethanes have been reviewed.

Although long-chain alkyl methacrylates show side-chain crystallinity having side chains with 12 carbon atoms or longer, only lauril methacrylate (LMA) has been polymerized by atom transfer radical polymerization (ATRP), which is a controlled/living radical polymerization (CRP) technique. Recently, Çayli and Meier polymerized fatty acid containing methacrylates using ATRP to prepare FA based polymers with targeted molecular weights, narrow polydispersity index (PDI) and specific chain end structures.

The RAFT polymerization is the most versatile CRP technique compared to the other CRP methods (ATRP and nitroxide-mediated radical polymerization), and RAFT technique is applicable to a wide range of monomers, initiator functionality, solvent composition and temperatures. Also, RAFT made polymers are better candidates for biological and pharmaceutical applications compared to ATRP generated macromolecules. Alkylmacro-RAFT agents have been used to prepare acrylic and coacrylic–alkyd block copolymers via RAFT technique. Recently, sustainable thermoplastic elastomers derived from fatty acids have been reported using RAFT method. Among the various FA’s, only the LMA have been polymerized by RAFT. Herein, we report the systematic RAFT polymerization of various fatty acid derived monomers in the presence of a free radical initiator 2,2'-azobisisobutyronitrile (AIBN) at 70 °C in tetrahydrofuran (THF) and 4-cyano-4-(dodecylsulfanylthiocarbonyl)sulfanylpentanionic acid (CDP) as the chain transfer agent (CTA) (Scheme 1). By adjusting the chain lengths of the fatty acids, polymers exhibit crystallinity. Polymer crystallinity is important since crystallinity affects their physical and mechanical properties such as storage modulus, permeability, density, stiffness, melting point, etc.

Experimental section

Materials

Fatty acids such as caprylic acid (CLA, ≥ 98%), capric acid (CRA, ≥ 98%), lauric acid (LA, 98%), myristic acid (MA, ≥ 99%), palmitic acid (PA, ≥ 99%) and stearic acid (SA, ≥ 95%) were...
The thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/SDTA 851e instrument at a heating rate of 10 °C min⁻¹ in N₂ atmosphere.

**Synthesis of FAMA monomers**

The monomers from various fatty acids (FAMA), such as caprylic (CLAMA), capric (CRAMA), lauric (LAMA), myristic (MAMA), palmitic (PAMA) and stearic (SAM) were synthesized as follows. In a typical example, CLA (0.104 mol, 15.0 g) and DMAP (0.0104 mol, 1.27 g) were dissolved in 50 mL dry DCM in a 250 mL double neck round bottom (RB) flask equipped with a magnetic stir bar. The RB flask was kept on ice-water bath and dry N₂ gas was purged through it. In a separate vessel DCC (0.1144 mol, 23.60 g) was dissolved in minimum volume of DCM and was added to the reaction mixture. Then, HEMA (0.1040 mol, 13.53 g) was added drop-wise for 30 min. The ice-water bath was removed after 30 min and the resulting mixture was stirred for 24 h at room temperature. After 24 h, the reaction mixture was filtered and 80 mL distilled water was added to the filtrate. The organic layer was further washed with saturated NaHCO₃ (120 mL × 4) followed by brine solution (100 mL × 2) and dried over anhydrous Na₂SO₄. The solvent was removed by rotary evaporator and purified by column chromatography using silica gel as stationary phase and hexanes- EtOAc (95 : 5, v/v) as an eluent to obtain CLAMA (yield: 75%); 1H NMR (Fig. S1†, 500 MHz, CDCl₃, TMS): δ (ppm) = 6.12 and 5.58 (C=CH₂, 2H, d), 4.32 (OCH₂CH₂O, 4H, t), 2.32 (O=CCH₂, 2H, t), 1.61 (O=C-CCH₂, 2H, m), 1.28 (–CCH₂–CCH₂CH₃CH₃, 8H, m), 1.94 (CH₂=CHCH₃, 3H, s), 0.87 (–CH₂CH₃, 3H, t); ESI-MS (Fig. S2†) of CLAMA: calculated m/z for [M + Na⁺]: 279.167, observed 279.323.

Similarly, CRAMA, LAMA, MAMA, PAMA and SAMA were synthesized by following the above procedure (Table S1†).

**Instrumentation**

Gel permeation chromatography (GPC) was used to obtain molecular weights and molecular weight distributions (polydispersity index, PDI) of polymers and the GPC instrument contains a Waters 515 HPLC pump, a Waters 2414 refractive index (RI) detector and two columns (Styragel HT4 and Styragel HT3) in THF at 30 °C at 1.0 mL min⁻¹ flow rate. The instrument was calibrated by using poly(methyl methacrylate) (PMMA) standards. The 1H NMR spectra were acquired in a Bruker Avance DM 500 spectrometer operating at 500 MHz. Positive mode electrospray ionization mass spectrometry (ESI-MS) was performed on a Q-Tof Micro YA263 high resolution (Waters Corporation) mass spectrometer. The UV-Vis spectroscopic study was carried out using a Perkin-Elmer Lambda 35 UV-Vis spectrophotometer. Rigaku Smart Lab powder diffractometer having Cu Kα = 1.54059 Å radiation was used for recording X-ray diffraction (XRD) spectra. Polarized optical microscopic studies were carried out using an Olympus CH 30 imaging microscope equipped with Image Pro Plus version 4.0 Software. Differential scanning calorimetric (DSC) studies were performed on a Mettler Toledo DSC1 STARE at 10 °C min⁻¹. Polymers were first cooled from room temperature to –70 °C, then heated to +120 °C and again cooled to –70 °C at 10 °C min⁻¹. The crystalline melting temperature (∆Tm) was taken from the third segment of the run i.e. from +120 to –70 °C, as the solvent or other volatile impurities would have evaporated on heating from –70 to 120 °C.
purged with dry N2 gas for 15 min. The reaction vial was put in a septa sealed glass vial equipped with a magnetic bar and 10.0 mg AIBN in 2.0 g THF) and 0.898 g THF were added to a 20 mL polymerization vial equipped with a magnetic bar and purged with dry N2 gas for 15 min. The reaction vial was put in a preheated reaction bath at 70 °C for 7 h. The reaction was quenched by cooling in ice-water bath, purified by reprecipitation in MeOH at least five times (from acetone solution) and dried under high vacuum at room temperature to obtain yellowish sticky polymer.

Synthesis of homopolymers via RAFT polymerization

In a typical example, CLAMA (0.78 mmol, 0.20 g), CDP (1.56 μmol, 6.29 mg), AIBN (3.1 μmol, 0.51 mg; 102 mg solution of 10.0 mg AIBN in 2.0 g THF) and 0.898 g THF were added to a 20 mL septa sealed glass vial equipped with a magnetic bar and purged with dry N2 gas for 15 min. The reaction vial was put in a preheated reaction block at 70 °C for 7 h. Then, the reaction was quenched by cooling in ice-water bath, purified by reprecipitation in MeOH at least five times (from acetone solution) and dried under vacuum at room temperature to obtain yellowish sticky polymer.

Chain extension reactions

CLAMA (100.0 mg, 0.390 mmol), PCLAMA macro-CTA (Mn,GPC = 7500 g mol⁻¹, PDI = 1.10, 117.0 mg, 0.0156 mmol), AIBN (3.1 μmol, 0.51 mg; 102 mg solution of 10.0 mg AIBN in 2.0 g THF) and 0.898 g THF were added to the 20 mL polymerization vial equipped with a magnetic stir bar and purged with dry N2 gas for 15 min. The reaction vial was put in a preheated reaction bath at 70 °C for 7 h, quenched by cooling in ice-water bath, and purified as mentioned above for the homopolymers.

Synthesis of block copolymers

MEO₂MA (0.5 mmol, 150.0 mg), PCLAMA macro-CTA (Mn,GPC = 7500 g mol⁻¹, PDI = 1.10, 0.150 g, 0.02 mmol), AIBN (4.0 μmol, 0.656 mg; 132.0 mg solution of 10.0 mg AIBN in 2.0 g THF), and THF (0.868 g) were added to a 20 mL polymerization vial equipped with a magnetic bar and purged with dry N2 gas for 15 min. The reaction vial was put in a preheated reaction block at 70 °C for 7 h. The reaction was quenched by cooling in ice-water bath and purified by reprecipitation in hexanes at least five times and dried under vacuum at room temperature to obtain yellowish sticky polymer. For PLAMA-b-PMEO₂MA, PMAMA-b-PMEO₂MA, PPAMA-b-PMEO₂MA and PSAMA-b-PMEO₂MA we used water as a non-solvent and block copolymers were lyophilized.

Results and discussion

Monomer synthesis

Side chain FA containing monomers were synthesized by esterification condensation of HEMA and fatty acids in the presence of DCC as coupling agent and DMAP as catalyst in DCM solvent at room temperature for 24 h. The FAMA monomers were obtained in high yields (74–85%, Table S1 of the ESI†) and structures were confirmed by ¹H NMR and mass spectroscopy. All the proton peaks have been assigned on their NMR spectrum (Fig. 1A for SAMA and more spectra in the ESI†). Experimental molecular masses obtained from ESI-MS study matched well with the theoretical molecular mass values (ESI-MS spectra in the ESI†). Also, FT-IR analysis of the monomers showed characteristic ester carbonyl group and the double bond CH₂=C(CH₃)₂ peaks. For example, stretching vibrations of the carbonyl C=O group and vinyl double bond in the FT-IR spectrum of CLAMA were observed at 1725 and 1638 cm⁻¹, respectively (figure not shown).

RAFT polymerization

FAMA’s are polymerized by RAFT method at 70 °C with CDP and AIBN in DMF and THF at [FAMA] : [CDP] : [AIBN] = 50/1/0.2. Although all the monomers are soluble in DMF (Table S2, ESI†), polymer from stearic acid (PSAMA) is insoluble in DMF. Polymers from caprylic acid (PCLAMA), capric acid (PCRAMA), lauric acid (PLAMA), myristic acid (PMAMA) and palmitic acid (PPAMA) are soluble in DMF. Therefore, we obtained low conversion and observed heterogeneous polymerization in DMF for SAMA (Table S3, ESI†). However, in THF all monomers and polymers are readily soluble and polymerizations proceed with a moderate rate (Table 1). The polymers exhibited narrow PDI (~1.25) and the number average molecular weight (Mn,GPC) determined from gel permeation chromatography (GPC) matches well with the theoretical molecular weights (Mn,tho) calculated based on monomer conversion. The resulting polymers showed symmetrical GPC peaks without shoulder and tailing (Fig. S12 of the ESI†). Note that Mn,GPC’s are apparent values relative to poly(methyl methacrylate) (PMMA) standard. Surprisingly, Mn,GPC and Mn,tho values matches well although hydrodynamic volume of PMMA standards are expected to be

Fig. 1 The ¹H NMR spectra of (A) SAMA, (B) PSAMA and (C) PSAMA-b-PMEO₂MA in CDCl₃.
different compared to the compact FAMA-based polymers. Demetriou and Krasia-Christoforou also showed excellent agreement between \( M_{n,GPC} \) and \( M_{n,\text{theo}} \) for the RAFT polymerization of LMA.\textsuperscript{17}

The PFAMA polymers showed expected absorption for tri-thiophosphate moiety at \( \lambda_{\text{max}} \sim 309 \) nm, indicating retention of the CTA group during RAFT polymerization. We determined number-average molecular weight (\( M_{n,\text{GPC}} \)) by this method.\textsuperscript{18} The \( M_{n,\text{UV-Vis}} \) matches nicely with the \( M_{n,GPC} \) and \( M_{n,\text{theo}} \) values (Table 1).

Polimerizations kinetics of FAMAs were also studied at different monomer (M) to CDP ratios ([M]/[CDP]), while keeping constant molar ratios of [CDP]/[AIBN] = 5 : 1. For all the monomers, unimodal GPC refractive index traces without shoulder and tailing confirming no bimolecular terminations during the polymerization for conversions up to \( ca. 87 \% \) for [M]/[CDP] ratios between 25 and 100 (Fig. 2A and B). Fig. 2C and D show that the \( M_{n,GPC} \) increases linearly with the increase of monomer/CDP ratio with narrow PDI (1.10–1.34) indicating the feasibility to control the molecular weight of poly(FAMA) (PFAMA) with the alteration of [M]/[CDP] (also see Table S4 and Fig. S12 of the ESL). By replacing CDP with CTP while keeping all other reaction conditions constant, we observed reasonable agreement between \( M_{n,GPC} \) and \( M_{n,\text{theo}} \) values with narrow PDI and GPC RI traces without shoulder and tailing (Tables S5, ESL). Generally, CDP and CTP are excellent CTA for the preparation of well-defined methacrylate polymers,\textsuperscript{19} and the above results indicate that both CDP and CTP can be used for the controlled RAFT polymerization of FAMA.

### Chain extension and block copolymerization

In the next stage, additional confirmation for the living nature of the polymerizations and possibility of block copolymer synthesis are examined. The resulting PFAMA homopolymers are used as macroCTA’s for the chain extension and block copolymerization with FAMA and MEO2MA, respectively, at [FAMA or MEO2MA]/[PFAMA-macroCTA]/[AIBN] = 25 : 1 : 0.2 in THF at 70 °C. The results are shown in Table 2 and Table S6 of ESL,\textsuperscript{1} where \( M_{n,GPC} \) values are in good agreement with the \( M_{n,\text{theo}} \) values determined from conversion data. Also, unimodal RI traces of chain extended homopolymers (PFAMA-b-PFAMA) and block copolymers (PFAMA-b-PMEO2MA) moved towards the higher molecular weight region with respect to the original macroCTA without any noticeable bimolecular termination products or unreacted macroCTA (Fig. 3 and S13 in ESL). Successful chain extension and block copolymerization confirmed end group retention with controlled molecular weight and narrow PDI.

The \( ^1H \) NMR technique was used to determine the chain-end structure and absolute molecular weights of PFAMA (Fig. 1B), PFAMA-b-PFAMA and PFAMA-b-PMEO2MA (Fig. 1C). Various proton peaks from the main chain repeating unit are assigned on the spectra. In addition, we observed a peak at 3.20 ppm corresponding to the –S–C(=S)–CH₂–C₆H₄ fragment protons and signals at 2.39–2.62 ppm from HOOC–CH₂–CH₂–C(=S)–CH₃ moiety in the chain ends of the polymer.\textsuperscript{22} Comparison of the integration areas from the terminal resonance signal at 2.39–2.62 ppm (4H) and the repeating unit protons at 4.04–4.41 ppm from the side chain –O–CH₂–CH₂–O–protons (4H) allowed calculation of the number-average molecular weight (\( M_{n,\text{NMR}} \)) from the NMR spectroscopy (Table 1 and S6). The NMR spectra of the block copolymers in CDCl₃ confirmed the presence of the peaks associated with each block. The integration ratios of main chain protons from PMEO2MA segment at 3.39 ppm to the CTA methylene protons at 2.39–2.62 ppm were used to calculate the degree of polymerization (\( D_p \)) for the PMEO2MA block. The \( D_p \) values in combination with the molecular weights of macroCTA’s allowed determination of the \( M_{n,\text{NMR}} \) of block copolymers. Good agreement between the \( M_{n,\text{theo}} \), \( M_{n,\text{NMR}} \), and \( M_{n,GPC} \) suggests controlled RAFT polymerization with the polymer chain ends having the fragments of CTA as expected according to the general mechanism of the RAFT technique.

### Thermal properties

Thermal degradation studies under nitrogen atmosphere using TGA studies confirmed thermal stability of PFAMA polymers up to \( ca. 175 \) °C (Fig. 4A). The first stage between 175 and 245 °C could be attributed to the decomposition of thiophosphate functionality in polymer chain ends. The mass loss in this region is substantially higher for PCRAMA and PCLAMA than that expected on the basis of loss of the end group alone, although in these polymers contribution from chain ends are higher compared to other PFAMA’s. Above 245 °C, side-group decomposition of monomer units and residual chain degradation takes place.\textsuperscript{20} Since ATRP made poly(lauryl methacrylate) (PLMA) showed melting point (\( T_m \)) of \(-34 \) °C,\textsuperscript{9} thermal properties of PFAMA

#### Table 1: Polymerization of FAMA’s in THF at 70 °C

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Conv. (%)</th>
<th>( M_{n,\text{GPC}} ) (g mol(^{-1}))</th>
<th>PDf</th>
<th>( M_{n,NMR} ) (g mol(^{-1}))</th>
<th>( M_{n,\text{UV-Vis}} ) (g mol(^{-1}))</th>
<th>( M_{n,\text{theo}} ) (g mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CLAMA</td>
<td>78</td>
<td>10 000</td>
<td>1.13</td>
<td>13 000</td>
<td>12 500</td>
<td>10 400</td>
</tr>
<tr>
<td>CRAMA</td>
<td>79</td>
<td>13 100</td>
<td>1.14</td>
<td>13 800</td>
<td>12 800</td>
<td>11 600</td>
</tr>
<tr>
<td>LAMA</td>
<td>73</td>
<td>14 600</td>
<td>1.17</td>
<td>12 500</td>
<td>13 200</td>
<td>11 800</td>
</tr>
<tr>
<td>MAMA</td>
<td>75</td>
<td>15 500</td>
<td>1.19</td>
<td>14 200</td>
<td>15 900</td>
<td>13 200</td>
</tr>
<tr>
<td>PAMA</td>
<td>81</td>
<td>16 000</td>
<td>1.16</td>
<td>19 300</td>
<td>17 100</td>
<td>15 300</td>
</tr>
<tr>
<td>SMA</td>
<td>82</td>
<td>18 500</td>
<td>1.15</td>
<td>18 800</td>
<td>19 200</td>
<td>17 200</td>
</tr>
</tbody>
</table>

\( ^{a} \) [FAMA]/[CDP]/[AIBN] = 50/1/0.2; time = 7 h. \( ^{b} \) Determined gravimetrically based on monomer feed. \( ^{c} \) Measured by GPC. \( ^{d} \) Obtained from \(^1H \) NMR.

Determined by UV-Vis study. \( ^{f} \) \( M_{n,\text{theo}} = ([\text{FAMA}]/[\text{CDP}] \times \text{molecular weight (}M_{a}\text{ of FAMA \times conversion}) + (\text{}M_{a}\text{ of CDP})\).
homopolymers were examined by DSC. Fig. 4B shows DSC thermograms of PFAMA homopolymers at 10 °C min⁻¹ heating rate under nitrogen atmosphere, demonstrating $T_m$ of approximately 12, 33, and 47 °C for PMAMA, PPAMA and PSAMA, respectively. Similar increase of $T_m$ with increasing alkyl chain lengths in the fatty acid containing polymers are reported, where polymers were prepared using ATRP of fatty acid based methacrylate monomers prepared from the reaction of methacryloyl chloride and fatty alcohols in diethyl ether. Increasing side chain crystallization is expected with the increasing alkyl chain lengths on the basis of symmetry and regularity even in the absence of strong intermolecular forces. Interestingly, we did not observe any $T_m$ for PLAMA although PLMA from ATRP and double-grafted cylindrical brushes with PLMA as the side chains showed $T_m$. This could be due to the presence of extra $-\text{CH}_2-\text{CH}_2-O-$ flexible unit in PLAMA compared to PLMA, which prevent crystallization of side chains. Note that we could not determine the degree of crystallinity from DSC study because of unavailable heat of fusion data for the perfect crystal.

### Crystalline morphologies of polymers

Crystalline structure was further examined by small-angle X-ray scattering (SAXS, Fig. 5A) and wide-angle X-ray scattering (WAXS, Fig. 5B) techniques. The SAXS profile of PSAMA ($2\theta = 2.52^\circ$) and PPAMA ($2\theta = 2.62^\circ$) show sharp peak (with multiplicity) indicating well-ordered structure formation. However, the scattering peak for PMAMA ($2\theta = 2.70^\circ$) and PLAMA ($2\theta = 2.89^\circ$) is very broad. A second scattering peak at $2\theta = 5.04^\circ$ and 5.24° for respectively PSAMA and PPAMA were observed. These $2\theta$ values are exactly double than the first $2\theta$ peaks,
indicating lipid lamellar structure. A crystalline phase of the lamella may be formed due to the interactions of the alkyl chains in the side chain. As expected, the long spacing ($d$) decreases with decreasing chain length of the fatty acid and we have determined $d$ values of 35.0, 33.7, 32.7 and 30.4 Å for PSAMA to PPAMA, PMAMA and PLAMA, respectively. A bilayer crystalline structure with a repeat distance of 40.8 Å is reported for stearic acid. The $d = 35.0$ Å for PSAMA indicates formation of different crystal structure than for only stearic acid due to the main chain methacrylate backbone with flexible $-\text{CH}_2-\text{CH}_2-O$ side chain units. However, above SAXS results provided lamellar structure for PSAMA, PPAMA, PMAMA and PLAMA.

The effect of fatty acid chain length on crystallinity is also seen from the WAXD plots in Fig. 5B. The peaks around $2\theta = 18.9^\circ$ ($d = 4.68$ Å) in the WAXD plot in Fig. 5B for PSAMA, PPAMA, PMAMA and PLAMA indicate the amorphous halo. PSAMA and PPAMA show a sharp peak ($2\theta = 21.47^\circ$, $d = 4.13$ Å) in addition to the broad peak, where the sharp peak is due to the crystallinity in those two polymers. Because of higher percentage of crystallinity in PSAMA as noticed in WAXS, the $d$ spacing between two lamellas is distinct as observed from SAXS. Increasing side-chain length helps crystalline domain formation due to the hydrophobic interaction among the large alkyl chains. Also, polarized optical microscopy images of PSAMA and PPAMA (Fig. 6) showed a birefringent texture distinctive of semicrystalline linear polymer chains, which melts and become isotropic when heated above their $T_m$.27

![Fig. 3](image-url) GPC RI traces of the (A) PCRAMA-macroCTA, chain extended PCRAMA-b-PCRAMA and block copolymer PCRAMA-b-PMEO$_2$MA; (B) PSAMA-macroCTA, chain extended PSAMA-b-PSAMA and block copolymer PSAMA-b-PMEO$_2$MA.

![Fig. 4](image-url) TGA thermograms (A) and DSC curves (B) of various side chain fatty acid-containing polymers under N$_2$ at a heating rate of 10 °C min$^{-1}$.

![Fig. 5](image-url) (A) SAXS and (B) WAXS patterns of various PFAMA's.
self-assembly potential of the well-de
amphiphilic random copolymers as unimer micelles.

By changing the alkyl chain length in the fatty acid, it is
renewable resources with unique properties for various
polymers (both random and block copolymers) can provide
the means to the construction of tailored materials from
different physical proper-
ties such as crystallinity and solubility. We are currently
extending our study to the design of fatty acid containing
fatty acid derived
macrocTAs for the preparation of block copolymers has also
been explored and PFAMA-
ff-PMEO2MA has been prepared.
In summary, we have demonstrated the RAFT polymerization
of fatty acid containing methacrylate monomers to prepare
fatty acid-based polymers with pre-determined molecular
weights and narrow PDI. The chain extension from PFAMA
macrocTAs for the preparation of block copolymers has also
been explored and PFAMA-b-PMEO2MA has been prepared.
By changing the alkyl chain length in the fatty acid, it is
possible to obtain materials with different physical properties
such as crystallinity and solubility. We are currently
extending our study to the design of fatty acid containing
amphiphilic random copolymers as unimer micelles.28 The
self-assembly potential of the well-defined fatty acid derived
copolymers (both random and block copolymers) can provide
the means to the construction of tailored materials from
renewable resources with unique properties for various
applications, such as controlled drug release and biocom-
patible materials.

Conclusion

In summary, we have demonstrated the RAFT polymerization
of fatty acid containing methacrylate monomers to prepare
fatty acid-based polymers with pre-determined molecular
weights and narrow PDI. The chain extension from PFAMA
macrocTAs for the preparation of block copolymers has also
been explored and PFAMA-b-PMEO2MA has been prepared.
By changing the alkyl chain length in the fatty acid, it is
possible to obtain materials with different physical properties
such as crystallinity and solubility. We are currently
extending our study to the design of fatty acid containing
amphiphilic random copolymers as unimer micelles.28 The
self-assembly potential of the well-defined fatty acid derived
copolymers (both random and block copolymers) can provide
the means to the construction of tailored materials from
renewable resources with unique properties for various
applications, such as controlled drug release and biocom-
patible materials.

Acknowledgements

We thank Department of Science and Technology (DST),
Government of India, India, for financial support [Project no.
SR/S1/OC-51/2010]. Binoy Maiti acknowledges Council of
Scientific and Industrial Research (CSIR), Government of India,
India, for the junior research fellowship.

Notes and references


