ORIGINAL CONTRIBUTION

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Synthesis and solution properties of comblike polymers from octadecyl methacrylate and acrylic acid

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Abstract Amphiphilic polymers consisting of a statistical distribution of octadecyl methacrylate (ODMA) and acrylic acid in respective molar ratios of 83–22 and 17–78 mol% and in a molecular-weight range of $2.35–4.70 \times 10^4$ gmol^{-1} have been synthesized. The series of polymers consisting of various mole fractions of ODMA and acrylic acid are expected to exhibit unique characteristics resembling ionomer to hydrophobically modified polyelectrolytes. The changes in the I_3/I_1 emission intensity ratios of pyrene, occurring in the presence of tetrahydrofuran (THF) solutions of the polymers have been taken as the main basis for inferring solution structures. The polymers are found to form random-coil to collapsed-coil/aggregated structures in THF solvent depending on the copolymer compositions. The polymer consisting of 83 mol% ODMA and 17 mol% acrylic acid behaves as an ionomer, capable of forming collapsed-coil structures at concentrations of 0.02 gml^{-1} and above as shown by a very high I_3/I_1 of 1.20 (I_3/I_1 of pyrene in THF is 0.85). In contrast, the poly(octadecyl methacrylate) homopolymer and the sets of copolymers consisting of a very high proportion of acrylic acid to an extent of 73 mol% and above contribute to almost negligible or very small changes in I_3/I_1 similar to the homopolymer, poly(octadecyl methacrylate), suggesting the formation of random-coil structures.

Keywords Comblike polymers · Copolymer of octadecyl methacrylate and acrylic acid · Solution properties in tetrahydrofuran · Fluorescence

Introduction

Amphiphilic polymers composed of hydrophilic and hydrophobic segments a exhibit characteristic tendency to undergo self-organization processes in the presence of solvents, forming superstructures on a mesomorphic scale [1, 2, 3, 4, 5, 6]. Such amphiphilic polymers prove more advantageous than simple surfactants in view of the diversity in the arrangements of the hydrophobic and hydrophilic segments, the length and branching of the hydrophobic tail, the molecular architecture afforded by varying the polymer geometry and, thus, enabling the formation of versatile mesophase structures. Different types of polymers, block copolymers [7, 8, 9, 10], stars, graft copolymers [11, 12, 13, 14, 15], segmented block copolymers [16, 17] and polysoaps [18, 19, 20, 21, 22, 23] contributing to the versatile molecular architecture with distinct subgroups provide classic examples of polymeric amphiphiles. The kinds of aggregated structures exhibited by a polymeric amphiphile, and arising from various kinds of forces, depend on the amphiphilic architecture and the polarity of the solvent. Polymeric amphiphiles, especially those consisting of ionizable comonomers, exhibit interesting solution properties. The solution

structures of these polymeric amphiphiles are controlled by various parameters, such as the ionic content of the polymers, the polarity of the solvent and the degree of ionization. These structures provide a molecular basis for understanding the kinds of forces controlling intramolecular and intermolecular association processes. Furthermore, they are also highly useful in understanding some significant phenomena, such as the ordering of lipids and the regulation of protein association/dissociation arising as a consequence of hydrophobic association inside biomembranes [24]. It is well known that polymers consisting of 15 mol% ionic comonomer or less are typically classified as ionomers. On the other hand, polyelectrolytes consisting of mainly ionic monomer residues, when hydrophobically modified (2–5%) exhibit unique rheological properties and find immense potential as thickening agents. Typically, an ionomer is capable of forming structures ranging from ionic clusters to hydrophobic aggregates similar to micellar assemblies, depending on the solubility of the backbone in the solvent under investigation and the polarity of the solvent. This has been well demonstrated in the solution behavior of many polymers, for example, polyurethane-derived ionomers [25]. Whereas in the case of hydrophobically modified polyelectroytes, similar aggregated structure formation occurs, depending on the nature of the solvent, as in case of ionomers, and the interplay between electrostatic interaction and the hydrophobic aggregation process mainly controls the solution structures. In this context, it becomes highly significant to investigate the solution structure of a set of polymeric amphiphiles consisting of various compositions of hydrophobic and hydrophilic comonomers in the chosen solvent. Such a set of polymers would cover a range of polymeric materials varying from ionomers to hydrophobically modified polyelectrolytes. Such studies are expected to throw useful light on the control of solution structures by the manipulation of ionic comonomer compositions.

Polymeric amphiphiles consisting of long side-chain and ionic monomers are currently drawing significant attention in view of their unique features. The long side-chain group provides surfactant-like structures capable of forming polysoap structures similar to micellar assemblies and contributes significantly to surface-energy modifications. The ionic comonomer, of course, controls electrostatic interactions. Kuo et al. [26] reported the synthesis of a low-molecular-weight copolymer of dodecyl methacrylate and acrylic acid. The polymer exhibits high polydispersity in its molecular weight and has been demonstrated to undergo typical aggregation processes in water at high pH. The copolymer has been successfully used in emulsion polymerization of styrene. The influence of the length of the side chain on the association properties, especially in an aqueous medium, has been well demonstrated using polymeric amphiphiles

derived from acrylic acid. It has been shown that polymeric gels consisting of a very low amount of the C_{18} side chain is capable of forming hydrophobic aggregates over a wide pH range, in contrast to similar polymeric systems consisting of side chains varying from C_8 to C_{12} [27]. The polymeric amphiphiles consisting of a C_{18} side chain thus become highly significant in view of the promotion of hydrophobic forces, in addition to crystalline properties. Recently, such kinds of polymers consisting of acrylic/methacrylic acid have been successfully used in miniemulsion polymerization of styrene [28]. In this study, we report the synthesis of four sets of polymeric amphiphiles consisting of octadecyl methacrylate (C_{18} side chain) and acrylic acid in mole percent ratio of 83:17, 45:55, 27:73 and 22:78 in a molecular-weight range $1–4\times10^4$ gmol^{-1}. These polymers do not exhibit solubility in an aqueous medium, especially at low pH. We chose to investigate the solution behavior of these polymers in a nonpolar solvent, namely tetrahydrofuran (THF) (dielectric constant, 7.5). THF is a very common solvent in molecular-weight estimations using gel permeation chromatography (GPC) and also different application systems. The solution structure of these sets of copolymers were investigated in comparison to that of poly(octadecyl methacrylate) homopolymer of similar molecular weight in order to investigate the influence of acrylic acid comonomer on the solution structure. Various techniques, such as fluorescence spectroscopy, viscosity, light scattering and neutron scattering, are generally employed to investigate the solution behavior of polymeric amphiphiles. The fluorescence spectroscopy technique proves highly useful in investigations on the solution behavior of polymers. It is well known that the use of changes in the fluorescence behavior of an external fluoroprobe, like pyrene, in the presence of polymer solutions can throw light on the microenvironment of polymer solutions [29]. In this study, the changes in the emission characteristics of a fluoroprobe, like pyrene, in THF solutions of the ionomers investigated were taken as the main evidence for probable changes in the microenvironment of polymer solutions arising as a consequence of specific organization processes.

Experimental

Materials

Octadecyl methacrylate, azobis(isobutyronitrile) (AIBN), both from Aldrich, USA, and ethyl methyl ketone (EMK) from Sisco Laboratories, Mumbai, India, were used as received. The acrylic acid (Sisco Laboratories) used in the polymerization reactions was purified by distillation. The high-performance liquid chromatography (HPLC) grade THF used in the fluorescence experiments was from S.D. Fine Chemicals, India. The solvents, petroleum ether and methanol employed in the isolation of the polymers were of Analar grades and were obtained from Glaxo, Mumbai, India.

Synthesis of the ionomers

The set of polymers consisting of a statistical distribution of non-polar octadecyl methacrylate and polar acrylic acid were synthesized by employing a solution free-radical-polymerization technique. Typically, to a stirred homogenous solution of octadecyl methacrylate (0.98 mol) in EMK, acrylic acid (0.46 mol) and AIBN (1% on monomer weight) were added. The reaction was performed by heating the mixture at 60 °C under continuous stirring. By this 65% conversion was achieved in all the polymerization reactions. The ultimate polymer was isolated using a nonsolvent. The nonsolvent used was either methanol or petroleum ether, depending on the acrylic acid content in the copolymer. For polymers with an acrylic acid content of more than 55 mol%, petroleum ether performed as an efficient nonsolvent medium, as against methanol employed for the kinds of polymers with an octadecyl component above 27 mol%. The polymers were ultimately dried in a vacuum at room temperature. Previous synthetic procedures for the kinds of copolymers of acrylic acid with octadecyl methacrylate or dodecyl methacrylate, invariably involved the use of 1:4 dioxane solvent in the presence of a chain-transfer agent, and resulted in low-molecular-weight polymers with molecular weights of about 10^3 gmol^{-1}.

Characterization of the polymers

The polymers were characterized using spectroscopic and GPC techniques. GPC measurements were carried out using a GPC 440 water chromatograph fitted with ultrastyragel columns (10^3, 10^4, 10^5 Å) in THF solvent. The apparent molecular weights were calculated using polystyrene calibration. Molecular weight estimations were also performed by GPC using chloroform solvent, in order to investigate the interference of the solution structures in THF solvent on the GPC estimations. NMR measurements were performed using a Bruker MSL 300P (300 MHz) spectrometer using CDCl$_3$ as a solvent and tetramethylsilane as an internal standard. Fourier transform IR spectroscopic analysis was carried out using a KBr mulling technique with a PerkinElmer spectrometer. The compositions of the ionomers were determined from the acrylic acid content in the ionomer, estimated from pH titration using alcoholic sodium hydroxide as a titrant.

Steady-state fluorescence measurements were performed with a Hitachi model 650-40 fluorimeter using an excitation wavelength of 337 nm. The change in the emission intensity ratio, I_3(385 nm)/I_1(377 nm), was used to monitor the possible changes in the micropolarity of the pyrene probe in the presence of the ionomer investigated. Fluorescence measurements were performed by employing an effective concentration of 1×10^{-6} M pyrene, the external probe. The stock solution of polymer, 0.1 gml^{-1} was diluted with HPLC grade THF to prepare the respective polymer solutions with concentrations ranging from 0.0005 to 0.008 gml^{-1}. All the fluorescence measurements were carried out at ambient temperature, 25 °C.

Results and discussion

Characterization of the ionomers

The structural representations of the homopolymer PODMA and the copolymer of octadecyl methacrylate and acrylic acid are presented in Fig. 1a and b, respectively. The ^{1}H NMR spectrum of the copolymer shows the complete removal of unreacted monomer and the occurrence of polymerization through double bonds as
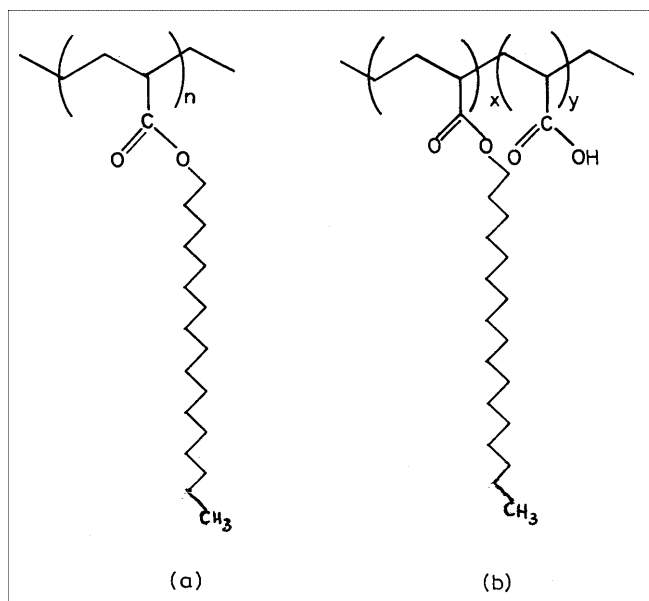

Fig. 1 Structural representation of **a** homopolymer of octadecyl methacrylate (*PODMA*) and **b** copolymer of octadecyl methacrylate and acrylic acid

shown by the absence of vinyl peaks at 5.5–6.5 ppm. The peak assignments for the ionomers are as follows: δ: 0.86–0.90 ppm, end CH$_3$ of the octadecyl side chain; 1.24–1.45, –CH$_3$ of the methacrylate group in the octadecyl methacrylate comonomer; 1.52–1.76 ppm, >CH$_2$ groups of the octadecyl side chain; 2.0–2.24–2.30 ppm, >CH$_2$ group of the backbone chain; 3.61–4.01, α >CH$_2$ groups of the side chain of octadecyl methacrylate and >CH group of the backbone. The IR spectral assignments of the ionomer are as follows: 3,490–3,500 cm^{-1}, –OH of –COOH; 2,955 cm^1, >CH$_2$ of the backbone chain; 1,755 cm^{-1}, >C=O of the comonomers. Similar spectral characteristics were observed for the other ionomers. The compositions of the copolymer estimated from the acid content are presented in Table 1 [28]. The characteristics of the copolymers synthesized in this laboratory and used for the present investigation are also presented in Table 1. Molecular-weight estimations of the set of polymers in both chloroform and THF solvents are presented. The homopolymer and the copolymers exhibit molecular weights in the range 2.35–4.69×10^4 in both chloroform and THF, the variations being ±20%.

Solution behavior of the ionic polymeric amphiphiles synthesized

Previous work on the correlation between the steric requirements of the polymer architecture and the solubility properties suggest that polymeric amphiphiles with a

Table 1 Chemical characteristics of comblike polymers

Polymer	Octadecyl methacrylate mole fraction in feed	Acrylic acid mole fraction in feed	Octadecyl methacrylate mole fraction in copolymer	Acrylic acid mole fraction in copolymer	Molecular weight ($\times 10^4$) in CHCl$_3$	Molecular weight ($\times 10^4$) in tetrahydrofuran
CP1	0.79	0.21	0.83	0.17	4.08	4.69
CP2	0.40	0.60	0.45	0.55	3.08	3.58
CP3	0.15	0.85	0.27	0.73	2.01	2.36
CP4	0.10	0.90	0.22	0.78	3.89	4.26

head geometry tend to form organized assemblies at the air/water interface [30] in contrast to those with a tail geometry, which exhibit considerable solubility in water. PODMA can be considered to represent the class of polymeric amphiphile with a head-type geometry in line with its tendency to exhibit negligible solubility in water and to form adsorbed monolayers at the air/water interface. The introduction of an ionic group, namely acrylic acid, to a different degree, is not expected to alter the geometry of the copolymer contributing to the solubility in water; however, it enables considerable changes in the solubility characteristics of the polymers, indicating changes in effective polarity characteristics. Thus, copolymers with an acrylic acid content above 55 mol% exhibit complete insolubility in a nonpolar solvent, like petroleum ether, unlike the homopolymer PODMA and the copolymers with an octadecyl methacrylate component above 27 mol%, which exhibit insolubility in a polar solvent, like methanol. However, all the copolymers and the homopolymer are readily dispersible in THF.

The copolymers under investigation composed of segments with different polarity characteristics and resembling a polymeric amphiphile are expected to undergo organization processes at a suitable solvent interface. In this study, the scope for such an organization process of the copolymers was investigated in THF solvent using a fluorescence technique employing pyrene as an external probe. Several reports [31] of fluorescence studies on ionomer membranes demonstrate the versatile application of pyrene in exploring the microenvironment of solutions. The rich vibronic structures in the fluorescence spectrum of pyrene are normally resolved in solutions and depend on the local polarity; and this is obvious from a comparison of the intensity ratio of the third (385 nm) to the first vibronic band at 377 nm in solvents of different polarity, for example, $I_3/I_1 = 2$ in perfluorinated solvent, 0.53 in dimethyl sulfoxide and 0.63 in water. The plot of the I_3/I_1 emission intensity ratio versus the concentration of the copolymers is shown in Fig. 2.

The emission intensity ratio is directly related to the average nonpolar characteristics of the microenvironment sensed by the pyrene probe. Pyrene exhibits an I_3/I_1 ratio of 0.85, in accordance with the reported value
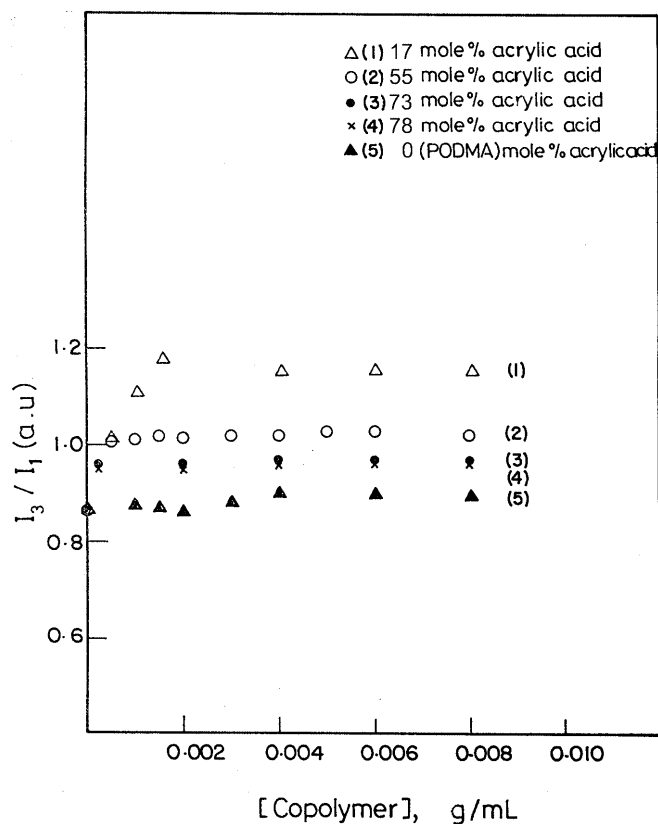

Fig. 2 Plot of I_3/I_1 emission intensity ratio versus concentration of copolymer consisting of 1–5, 0.17, 0.55, 0.73, 0.78 and 0.0 m acrylic acid in tetrahydrofuran (*THF*). The pyrene concentration was fixed at 1×10^{-6} M

within the limits of experimental error [29]. It is observed that pyrene exhibits a negligible change in the I_3/I_1 emission intensity ratio in the presence of octadecyl methacrylate homopolymer. The almost similar I_3/I_1 emission intensity ratio of pyrene probe in THF solvent (0.88) and THF solutions of homopolymer (0.85–0.89) clearly indicates the absence of aggregated structures. Further, it is observed that pyrene exhibits a small increase in the I_3/I_1 ratio from 0.85 to 0.97 in the presence of sets of copolymers consisting of 73 and 78 mol% acrylic acid, over a concentration range of 0.0005–0.008 gml^{-1}. This suggests that the introduction of the

polar acrylic acid component in the PODMA structure or rather the hydrophobic modification of poly(acrylic acid) in the range of about 25% tends to favor the formation of slightly aggregated structures, contributing to an increase in the nonpolar characteristics of the microenvironment. In contrast, in the case of polymers with an acrylic acid content of 55 and 17 mol%, an increase in the emission intensity ratio from 0.85 to 1.02 and 1.20, respectively, occurs. A significant rise in the emission intensity ratio occurs especially in case of the polymer with 17 mol% acrylic acid at concentration of 0.002 gml^{-1} and above. This suggests the formation of aggregated structures of polymers contributing to the nonpolar microenvironment of solubilized pyrene.

A comparative evaluation of the I_3/I_1 emission intensity ratios in THF solutions consisting of different mole percent ratios of acrylic acid suggests that the copolymer compositions play a predominant role in controlling the solution structures. The tendency to form aggregated structures contributing to the nonpolar microenvironment in the presence of a nonpolar solvent, like THF, increases in the presence of octadecyl methacrylate and acrylic acid in the optimum ratio of 83 and 17 mol%. The homopolymer octadecyl methacrylate and poly(acrylic acid) do not exhibit a tendency to form aggregated structures, as observed from the negligible change in the I_3/I_1 emission intensity ratio of pyrene. The behavior of the homopolymer in other nonpolar solvents, like chloroform and cyclohexane, to form random-coil structures is similar to that observed in THF. This is suggested from the very small changes in the I_3/I_1 emission intensity ratio of pyrene in the presence of homopolymer (PODMA) solutions in chloroform and cyclohexane solvent (Fig. 3). Although PODMA and poly(acrylic acid) exhibit solubility in THF, it is probable that the difference in the solubility properties and the solution structures of these polymers in THF accounts for the formation of the aggregated structures. However, it should be noted that the formation of such aggregated structures occurring at concentrations of 0.002 gml^{-1} and above does not contribute to great errors in molecular-weight estimations using GPC. The close agreement in the molecular-weight data of the set of copolymers (Table 1) estimated from GPC in chloroform solvent adds further evidence to this observation. The behavior of these kinds of polymers to undergo specific organization processes at the liquid/liquid interface has been employed in miniemulsion polymerization of styrene monomer to form polystyrene latex with particle size distributions in the range 100–250 nm [28].

The polymer consisting of 17 mol% acrylic acid can be considered to resemble an ionomer. Previous studies on typical ionomers from polystyrene sulfonate or polyurethanes suggest the formation of aggregated structures from ionic clusters in the presence of a nonpolar solvent, like THF. In agreement with this, the
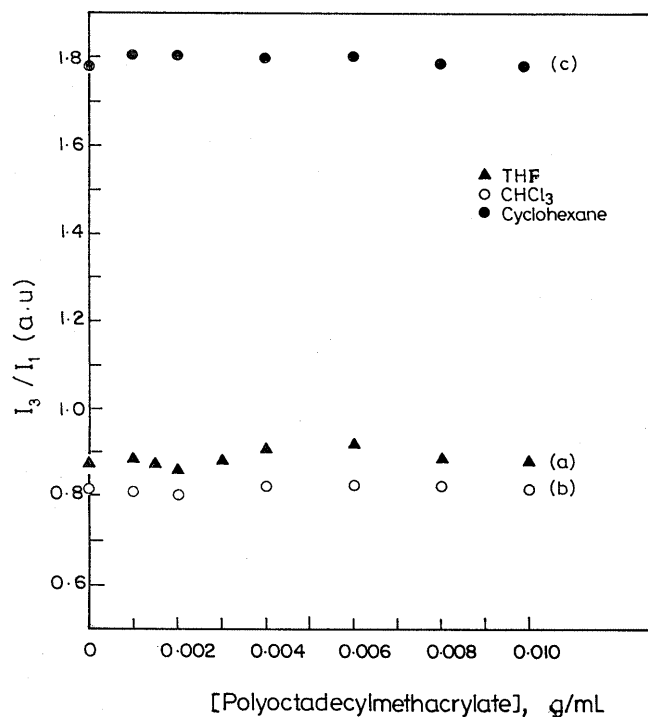

Fig. 3 Plot of I_3/I_1 emission intensity ratio of pyrene versus concentration of PODMA in THF (a), cyclohexane (b) and chloroform (c)

present investigation illustrates that the typical copolymer from octadecyl methacrylate consisting of an optimum concentration of 17 mol% acrylic acid exhibits aggregated structure formation at and above a critical concentration of 0.002 gml^{-1}. The beneficial properties of the aggregated structures of this typical polymer in various technological application systems could be realized only at concentrations of 2 gl^{-1} or higher. The aggregated structures however, do not interfere with characterization techniques, like GPC, as in such measurements, a very low concentration in the range of microgram levels is employed.

Conclusion

The polymeric amphiphiles consisting of a statistical distribution of octadecyl methacrylate and acrylic acid in a respective molar ratio range of 83–22 and 17–78 mol% investigated in this study provide simple systems exhibiting solution structures resembling ionomers to polyelectrolytes. The typical copolymer, consisting of 83 and 17 mol% octadecyl methacrylate and acrylic acid, behaves like an ionomer, exhibiting aggregated structures in the presence of THF solvent, as suggested from the nonpolar microenvironment of the pyrene probe exhibiting a considerable increase in

the I_3/I_1 emission intensity. Interestingly, the homopolymer, PODMA or the copolymers consisting of more than 72 mol% acrylic acid contribute only negligibly to changes in the micropolarity of pyrene, suggesting there is scope for the formation of random-coil structures. The control of the solution structures in THF solvent ranging from random-coil to aggregated-coil structures by copolymer composition has been demonstrated.

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