Functionalized Polymers Derived from the Reaction of Polymaleic Anhydride with Amines and Alcohols

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Synopsis

In the present study the application of polymaleic anhydride as a reactive polymer is illustrated in its reactions with didodecylamine, diphenylamine, and dodecanol. These polymers consisting of lipophilic segments (originating from the long aliphatic chains) or of the mesomorphic diphenyl moiety coupled with the polar carboxylic or carboxylate group can in principle exhibit mesomorphism in the melt and aggregate in dispersion. Of these derivatives didodecyl derivative froms mesomorphic-like structure in the melt, dodecanol monoester derivative dissolves freely in water whereas the sodium salts of the polymers disperse in water due to the presence of distinct polar and lipophilic moieties in their molecules.

INTRODUCTION

The reaction of maleic or succinic anhydride with long-chain aliphatic amines, in 1:1 molar ratio, for instance, dodecylamine or didodecylamine, resulted in the synthesis of derivatives of succinamic and maleamic acids, respectively, whose salts formed in water micelles[1] or vesicles.[2] In addition the same salts exhibited in the melt mesomorphic-like behavior.

Maleamic acid sodium salt derivatives as well as salts of the corresponding monoesters of maleic acid can, in principle, be subjected to polymerization. The polymerization may be affected if it were performed in concentrations exceeding their cmc due to topochemical effect exercized by the aggregation-organization of the monomers. A preferred mode, however, would be to homopolymerize maleic anhydride first and then to functionalize this polymer upon reaction with appropriate amines or alcohols. The method is, of course, of general applicability since the anhydride group can react with any primary or secondary amine or alcohols affording polymaleamic acid derivatives or monoesters of polymaleic acid. Evidently various products may be obtained, such polymers resulting from the neutralization of the carboxylic group by inorganic or organic bases or by esterification of the same functionality. In addition copolymers may result upon reaction of polymaleic anhydride with more than one amine or alcohol. In the present study the application of polymaleic anhydride, as a reactive polymer, is illustrated with its reaction with didodecylamine, diphenylamine, and dodecylalcohol. To our knowledge this is the first time that polymaleic anhydride is used as a reactive polymer

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for the synthesis of functionalized polymers. In addition to this, we also study the structural requirements for the exhibition of mesomorphic character by these polymers.

EXPERIMENTAL

Polymerization of Maleic Anhydride. Sublimed maleic anhydride, dissolved in dry acetic anhydride, was polymerized by γ-rays, in a Cobalt-60 source under the conditions employed by Lang et al.[3] A total dose of 43 Mrad was used.

PMAH–Didodecylamine. In dry acetone, 0.01 mol of polymaleic anhydride (corresponding to monomer), was dissolved. To this solution 0.01 mol of didodecylamine was added and the solution refluxed for several hours. The precipitated material was dissolved in ethylacetate and reprecipitated with acetone twice.

PMAH–Diphenylamine. Polymaleic anhydride was dissolved in dry acetone and reacted with diphenylamine at room temperature. The solvent was distilled off and the remaining material was redissolved in an acetone: acetonitrile (1 : 1) mixture and reprecipitated with hexane.

PMAH–Dodecanol. The reaction was performed in dry acetone. The precipitated material was dissolved in ethyl acetate and reprecipitated with pentane.

The functionalization of polymaleic anhydride was a facile process and the introduction of the respective groups was established with NMR spectroscopy. Optical microscopy was performed using a Reichert "Thermopan" polarizing microscope. Differential scanning calorimetric studies were done in a DuPont 910 apparatus. Number average molecular weight of the starting material, i.e., of polymaleic anhydride, was determined employing a Knauer vapor pressure osmometer. Isobutylmethyl ketone was employed as solvent, at 54°C, and the molecular weight was found approximately 7000. Proton NMR spectra were recorded on a Varian FT80 spectrometer operating at 80 MHz. The probe temperature was 34°C and solutions of 10% w/v in DMSO-d_6 were used.

RESULTS AND DISCUSSION

The belief that maleic anhydride, due to steric hindrance of its double bond, cannot be homopolymerized is widely accepted among polymer chemists and this was probably the reason for the limited research activity concerning the polymerization of this monomer. It has, however, been reported that maleic anhydride was homopolymerized by the action of γ-rays,[3] free radical catalysts[4-14] at high concentrations, and organic bases.[16] The homopolymerization of maleic anhydride was reviewed by Gaylord.[17] Polymaleic anhydride is reactive and susceptible to react with amines and alcohols. The polymers prepared by reacting polymaleic anhydride with didodecylamine, diphenylamine, and dodecanol are shown in the scheme below:
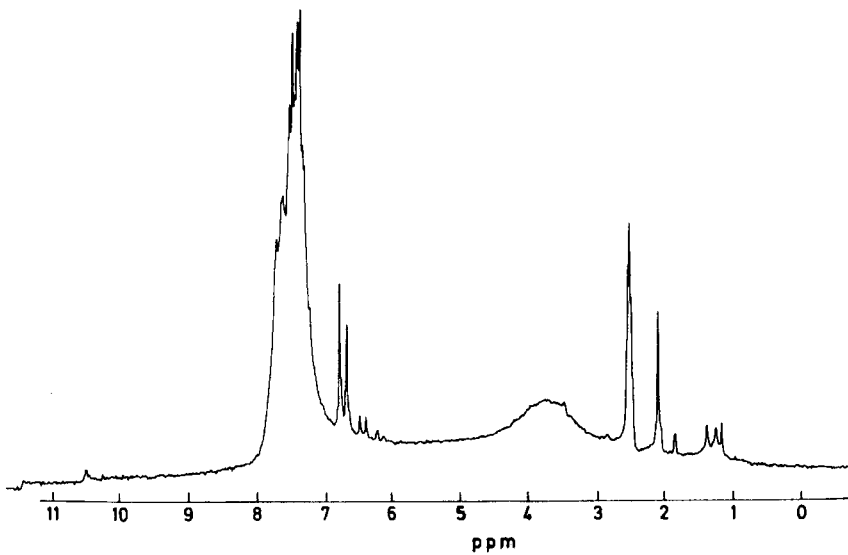
Scheme

The structure of the polymers was confirmed by proton NMR spectroscopy. Thus in Figures 1–3 the proton NMR spectra of polymers I, II, and III are shown and in Table I the ^{1}H chemical shifts are summarized. The peaks of n-alkyl groups at δ 0.85(CH_3),1.24(CH_2)$_n$,3.13,3.16 for the α-CH_2 and 2,61,2.85 for backbone protons of n-dodecanol and didodecyl derivatives, respectively, the shoulder at δ 1.56(β-CH_2) and the peaks in the aromatic region in conjunction with results of integration clearly indicate that the amines and dodecanol have completely reacted with polymaleic anhydride to give the functionalized polymers.

Polymer I. This is the polymerized counterpart of N,N-didodecyl maleamic acid,[1] which showed mesomorphic behavior and formed vesicles in alkaline

Fig. 1. Proton NMR spectrum of polymer I.

Fig. 2. Proton NMR spectrum of polymer **II**.

media. The mesomorphic character of the polymer was established by DSC and optical microscopy. Thus, its multiple step melting is shown in Figure 4, in which the first peak is associated with the melting of the hydrocarbon chains whereas the second peak may be attributed to the breakage of hydrogen bonding between the carboxylic groups of two polymeric chains. A characteristic smectic-like texture of this polymer, obtained during its cooling
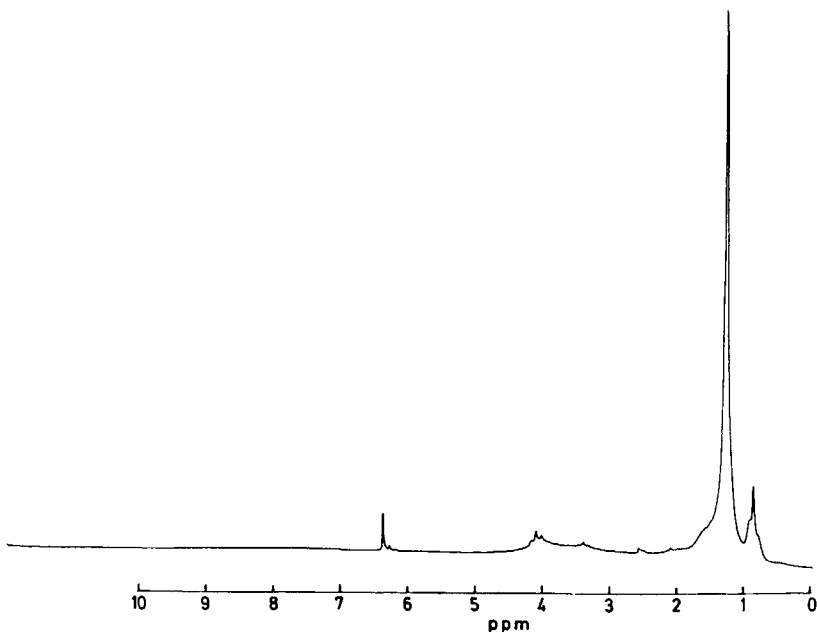

Fig. 3. Proton NMR spectrum of polymer **III**.

TABLE I
Proton Chemical Shifts[a] of Functionalized Polymers in DMSO-d_6 Solutions

Functional group	CH_3	$-(CH_2)_2-$	α-CH_2	β-CH_2	$-(CH-CH)-$	$-COOH$
$-NH[(CH_2)_{11}CH_3]_2$	0.85	1.24	3.16	1.55	2.85	9.11
$-NH-C_6H_4-C_6H_5$[b]					2.50	9.92
$-O(CH_2)_{11}CH_3$	0.84	1.24	3.13	1.56	2.61	

[a] In ppm from TMS.
[b] The aromatic protons absorb at: o-protons, δ 6.72; others, δ 7.20–7.69.

run, is shown in Figure 5 while in Figure 6 mesomorphic and crystalline phases exist simultaneously within the broad liquid crystalline phase due to the polydispersity of the polymer. On further heating the isotropic phase is destructed, at about 180°C, due to decarboxylation of the carboxylic group. The sodium salt of the polymer did not show mesomorphic behavior in the melt since it decomposed before reaching its high melting point. The same polymer salt was also dispersed in water ($10^{-2}M$) and it was examined for the formation of vesicles by a Siemens Elmiscope electron microscope. Vesicles were not, however, observed in contrast to its monomeric counterpart.[2] The polymer, however, did possess the structural features, i.e., the polar head coupled with two long aliphatic chains, for the formation of vesicles.

Polymer II. In this polymer the typical mesogenic biphenyl group was introduced in an attempt to induce mesomorphic character, at least, to the free polyacid since the sodium salt would certainly decompose before melting. However, decomposition did occur for both the acid (at 230–240°C) and salt. It is interesting to note, however, that the sodium salt of this predominantly aromatic polyacid disperses with sonication in water.

Polymer III. This polymer was prepared, under mild experimental conditions, by monoesterification of polymaleic anhydride with dodecanol. The free
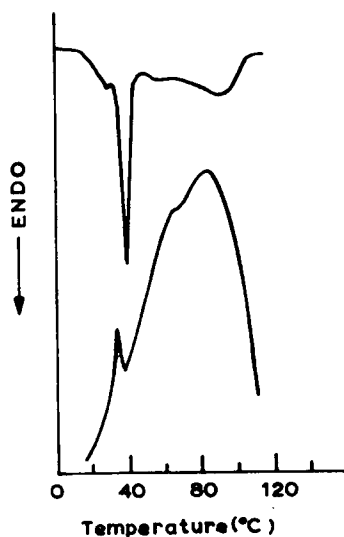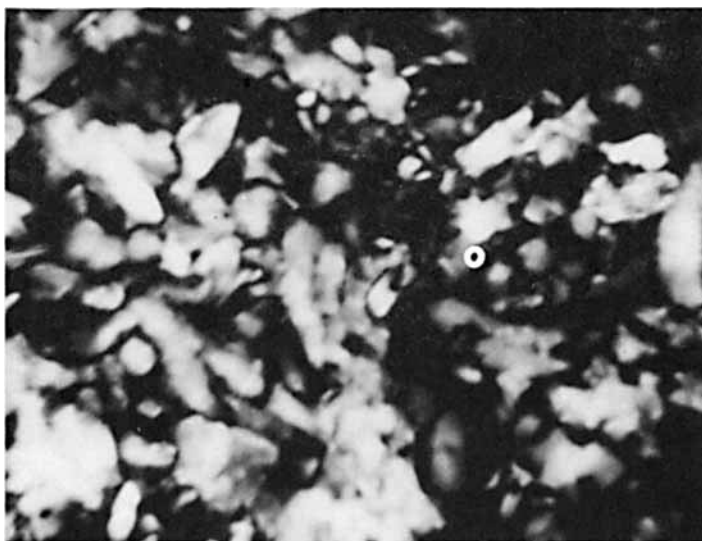

Fig. 4.   DSC diagram of polymer I.

Fig. 5.   Mesomorphic-like texture of polymer I obtained on cooling.

polyacid melted at about 125°C, with pressing of the cover slip during microscopic examination, to an amorphous material whereas its sodium salt decomposes at about 230°C before melting. Both the free polyacid and its sodium salt are water soluble while sonication is required to disperse the previously mentioned amide derivatives. Thus the replacement of amide by the ester group affects significantly the properties of these polymers to dissolve or disperse.

Fig. 6.   Mesomorphic-like and crystalline phases of polymer I observed on cooling.

Aromatic carboxylic acids form a well-known class of thermotropic liquid crystalline compounds.[18,19] The most numerous are p-substituted benzoic and cinnamic acids, biphenyl-2-carboxylic acids and 6-substituted naphthalene-2-carboxylic acids which form dimers through hydrogen bonding of their carboxylic groups. It is not, however, the case with n-aliphatic acids,[18,19] which are not mesomorphic and only the presence of double bonds, due to their polarizabilities, raise the intermolecular attractions and thus 2,4-nonadienoic acid is liquid crystalline. In the present study it is investigated whether the approach, by polymer bonding, of functionalized aliphatic acids contributes or not to the exhibition of liquid crystallinity. From the results obtained it is evident that, although polymerization certainly enhances intermolecular attraction, it simultaneously increases melting point and decarboxylation starts before the appearance of the mesomorphic phase. The introduction of the N,N-didodecyl moeity in polymer I lowers the melting point and results in the exhibition of mesomorphic phase which is also the case with its monomeric counterpart.[2] For the monoester the lack of hydrogen bonding between amide linkages lowers the melting point but at the same time leads to a freedom of the molecular chains, and therefore the formation of layer structure, which is responsible for the exhibition of liquid crystallinity, is not favored. Finally the diphenyl amide derivative melts at such a high temperature that decomposition of the polymer occurs before possible mesomorphic phase could appear. The dispersion of its sodium salt in water can be attributed to the relatively polar character exhibited by the diphenyl group.

In conclusion polymaleic anhydride constitutes a useful reactive polymer from which a series of functionalized polymers or copolymers may be prepared by mild reaction conditions. Specifically N,N-didodecyl maleamic acid derivative exhibited mesomorphic character which was attributed to a lamellar structure consisting of the lipophilic and polar portions of the polymer. The work is extended to include other homopolymers as well as copolymers prepared by the above investigated process.

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