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ADHESIVE LIQUID-CRYSTALLINE POLYMERS

René P. Nieuwhof, Antonius T.M. Marcelis, Ernst J.R. Sudhölter*

Laboratory of Organic Chemistry, Wageningen Agricultural University, Dreijenplein 8, 6703 HB Wageningen, The Netherlands

Maarten W.J. van der Wielen, Martien A. Cohen Stuart, Gerard J. Fleer

Laboratory of Physical and Colloid Chemistry, Wageningen Agricultural University, Dreijenplein 6, 6703 HB Wageningen, The Netherlands

Abstract: The synthesis and characterization of liquid-crystalline polymers with possible good adhesive properties is reported. These polymers are prepared by alternating copolymerization of maleic anhydride and mesogenic alkenes. The spacer length m is varied (m = 2, 3, 4, 6, 8 and 9) and methoxybiphenyl is used as the mesogenic group. The glass transition temperature decreases and the isotropization temperature increases with spacer length. Depending on the spacer length and temperature, S_B and S_{Ad} mesophases can be observed. After annealing, spin-coated films of these polymers show very regular layered structures with a layer spacing similar to that in the bulk.

INTRODUCTION

Since the introduction of liquid-crystalline polymers (LCPs), a tremendous amount of work has been done to synthesize and characterize novel polymers, study their properties, develop methods for processing and find new applications (Ref. 1). Until now, only little attention has been paid to LCPs with maleic anhydride moieties (MA) in the backbone (Ref. 2).

Copolymers containing MA moieties are known to show good adhesion to metals (Refs. 3, 4) and can be applied in corrosion protection (Refs. 4, 5, 6), which makes them attractive for coating applications. Due to the anhydride rings in the backbone, polymers are obtained with a high degree of stiffness and subsequently a high glass transition temperature. Alternating copolymers from MA can be synthesized by copolymerization with a variety of monomers that are able to form electron donor-acceptor complexes with MA, *e.g.* vinyl ethers, styrenes and alkenes (Ref. 7). LCPs with MA moieties can be obtained by copolymerization of MA

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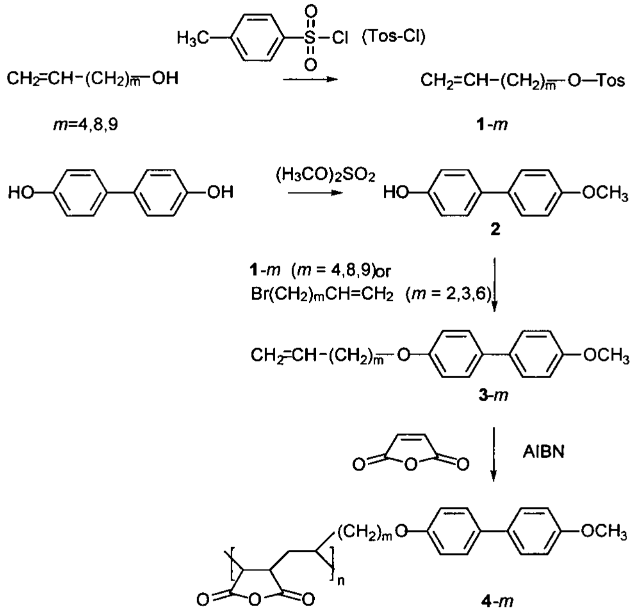
with these monomers carrying mesogenic moieties. This research is focused on the development and application of side-chain liquid-crystalline polymers (SCLCPs) with strong adhering groups that are able to form layered structures. The influence of spacer length on phase behavior and transition temperatures of SCLCPs from MA and mesogenic alkenes is described. The formation of thin ordered films has also been studied.

RESULTS AND DISCUSSION

Polymerization

Scheme 1 outlines the synthesis of compounds **1**-*m*, **2**, **3**-*m* and copolymers **4**-*m*. Copolymerizations are carried out in freshly distilled THF under argon atmosphere and initiated with AIBN. After precipitation, polymer yields varying from 20 to 90 % were obtained. FT-IR and ^{1}H-NMR signals correspond with the expected chemical structures. A complete description of the synthesis and characterization of monomers and polymers **4**-*m* will be published elsewhere (Ref. 8). Molecular weights of polymers **4**-*m* are determined by GPC and are listed in Table 1.



Scheme 1. Synthesis of monomers and polymers

Tab. 1. Characteristic data of polymers **4**-*m*. Number-average molecular weights (M_n), weight-average molecular weights (M_w), polydispersity indices (PDI), degrees of polymerization (DP) and yields

Polymer	10^{-3} M_n in g mol^{-1}	10^{-3} M_w in g mol^{-1}	PDI	DP	Yield in %
4-*2*	2.01	2.67	1.32	6	20
4-*3*	2.82	5.26	1.87	8	54
4-*4*	3.99	6.54	1.64	10	90
4-*6*	3.27	5.66	1.73	8	76
4-*8*	3.74	5.98	1.60	9	57
4-*9*[a]	3.37	5.32	1.58	7	74
4-*9*[b]	4.05	5.43	1.34	9	65

[a] first batch [b] second batch

Liquid crystalline properties of the polymers

Before thermal analysis, the polymers are dried over P_2O_5 at 100°C until FT-IR shows that all anhydride moieties are ring closed. Thermal properties of polymers **4**-*m* are investigated by Differential Scanning Calorimetry (DSC) and Polarized Optical Microscopy (POM). Tab. 2 displays the phase transition temperatures and the corresponding entropy changes, as determined by DSC. X-ray diffraction is used to identify the liquid crystalline phases. These measurements point out that polymers **4**-*8* and **4**-*9* form interdigitated S_A layers (S_{Ad}) with a layer spacing of 3.02 and 3.18 nm, respectively. From X-ray diffraction patterns below T_g a broad peak at 0.445 nm emerges, corresponding to hexagonal packing (S_B) of mesogens.

Tab. 2. Phase transition temperatures (corresponding heat capacity change or entropy changes in J/mol °C) and phase types of polymers **4**-*m*[a]

Polymer	transition temperatures in °C
4-*2*	G_I 119.7 (117) I
4-*3*	G_{Ad} 146.4 (123) S_{Ad} 170.4 (7.4) I
4-*4*	G_B 120 (-[b]) S_B 127.9 (7.1) S_{Ad} 136.3 (10.1) I
4-*6*	G_B 128.9 (112) S_B 139.8 (5.6) S_{Ad} 160.8 (8.1) I
4-*8*	G_B 103.4 (60.7) S_B 117.1 (5.7) S_{Ad} 155.9 (13.2) I
4-*9*[c]	G_B 98.9 (80.6) S_B 111.7 (3.7) S_{Ad} 164.3 (13.0) I
4-*9*[d]	G_B 100.8 (104) S_B 110.8 (3.3) S_{Ad} 164.5 (16.4) I

[a] I = isotropic phase, S_{Ad} = interdigitated smectic A phase, S_B = smectic B phase, G_X = glass phase, wherein X is the frozen in structure [b] could not be determined [c] first batch [d] second batch

The transition temperatures of polymers **4**-*m* as a function of spacer length are shown in Fig. 1. From this figure it is clear that T_g decreases with spacer length. For longer spacers there is a higher degree of decoupling between the polymer backbone and the mesogenic groups, leading to a higher overall flexibility of the polymer backbone. The transition from S_B to S_{Ad} mesophase closely follows T_g. Below m = 4, no S_B mesophase could be observed, due to coupled motions of the mesogens and the polymer backbone. The isotropization temperature (T_i) first decreases and then increases with spacer length, leading to a higher mesophase stability. This behavior has been observed before by Gemmel et al. (Ref. 9). For longer spacers, mesogens can move more independently from the polymer backbone. For m = 2 the orientation of the mesogens is probably hindered by the polymer backbone, preventing mesomorphic behavior.

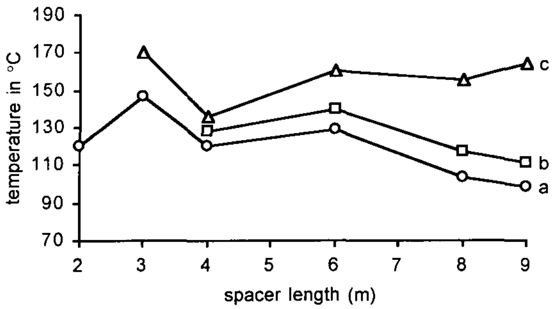


Fig. 1. Effect of spacer length on the transition temperatures: a=T_g; b=$T(S_B\text{-}S_{Ad})$; c=T_i

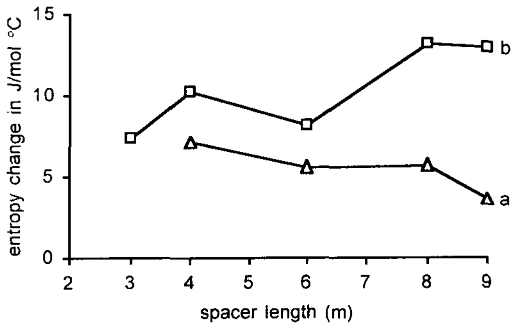


Fig. 2. Effect of spacer length on the entropy changes at a: $T(S_B\text{-}S_{Ad})$ and b: T_i

The change in entropy at T_i shows an increasing tendency with spacer length (Fig. 2), representing an increase in the degree of order. The change in entropy on going from S_B to S_{Ad}

mesophase slightly decreases with spacer length. The hexagonal packing may be induced to some extent by the presence of a stiff backbone, which is more pronounced for shorter spacers. Percec et al. (Ref. 10) stated that the highest degree of order is observed for LCPs with a stiff backbone.

Upon cooling from the isotropic melt, POM reveals for all polymers similar textures, except for polymer **4**-*2*. First a grainy texture is observed, which develops into small domains of band-like coloured textures after annealing in the LC phase for several days. Due to the high viscosity just above the glass transition temperature, no change in texture can be observed upon going from the S_{Ad} to the S_B mesophase.

Thin films of liquid crystalline polymers

The behavior of thin spin-coated films of polymers **4**-*4* and **4**-*9* on silicon wafers has been studied by van der Wielen et al. (Ref. 11). After annealing in the mesophase, these films show layered structures with a high degree of perfection. The electron density profile, as determined from the X-ray reflectivity pattern, is depicted in Fig. 3.

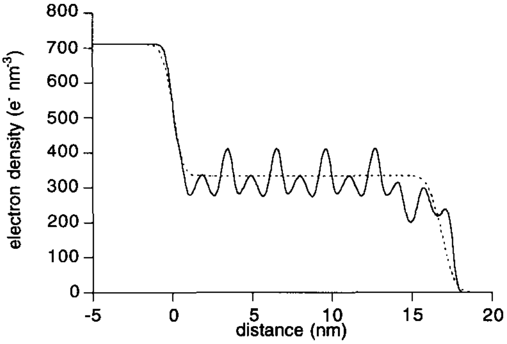


Fig. 3. Calculated electron density profile of a thin film of polymer **4**-*9*, as determined from the X-ray reflectivity pattern, as a function of depth. The dashed curve represents the electron density profile for the spin-coated film before annealing.

From the X-ray reflectivity pattern a layer spacing of 3.1 nm is calculated, which is in good agreement with the layer spacing of 3.18 nm in the bulk.

CONCLUSIONS

The synthesis and characterization of side-chain liquid-crystalline polymers from alternating copolymerization of maleic anhydride with mesogenic alkenes is presented. The temperature range of the mesophase increases with spacer length (m): the glass transition temperature decreases and the isotropization temperature increases. X-ray diffraction measurement reveals a high degree of order between the mesogens. Just above the glass transition temperature a smectic B (S_B) mesophase is found with a hexagonal packing of mesogens. Upon heating this transforms into an interdigitated smectic A (S_{Ad}) mesophase. Upon spin-coating of these polymers on silicon wafers and subsequent annealing in the mesophase, well-ordered films with a layer spacing corresponding to that of the S_{Ad}-mesophase in the bulk are observed. Based on the ability of maleic anhydride groups to show strong adhesion (Refs. 3, 4) and corrosion protection (Refs. 4, 5, 6) and the finding that highly ordered thin films of these polymers are formed after annealing, these polymers may be very attractive for coating applications.

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