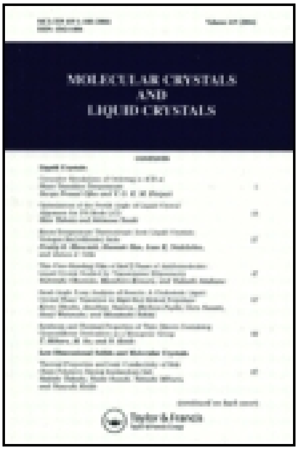

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Novel Liquid Crystal Admet Polymers with Banana Main-Chain Mesogens

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Novel Liquid Crystal Admet Polymers with Banana Main-Chain Mesogens

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*We prepared novel macromolecular architectures of main-chain polymers poly(**1**)–poly(**6**) by a ruthenium-catalyzed acyclic diene metathesis (ADMET) polymerization of banana diene monomers **1–6**. Copolymerization with a calamitic diacrylate monomer **7** yielded a copolymer poly(**1**-alt-**7**) in which the banana and the calamitic units regularly alternated along the polymer main chain. We also started the structural characterization of the polymers and found a varied mesophase behavior depending on the nature of the banana mesogen incorporated.*

Keywords: ADMET; banana mesogen; main-chain polymer; metathesis polymerization

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INTRODUCTION

Most examples of liquid crystalline polymers consist of calamitic mesogens which are directly incorporated into the polymer main chain, or attached to it as pendant side groups. In both cases, flexible spacer segments are commonly used to connect the mesogens within the polymer structure. Main-chain and side-group liquid crystal polymers offer nowadays a huge diversity of mesophase structures and transitions, and physical properties associated with them [1]. In contrast, very little is known of polymers containing banana mesogens at different sites of the polymer structure.

Certainly one of the most intriguing discoveries in soft matter in the last few years was the finding that banana-shaped molecules can assemble in layered chiral mesophases, even when not containing a chiral center in their molecular framework [2]. While, several classes of banana molecules have been synthesized [3], only very few polymers based on banana units are known [4–7]. Nevertheless, polymers are expected to add much value to their low-molar-mass counterparts. In fact, polymers from banana monomers could combine the unique properties of polymers with those peculiar to banana molecules. Specifically, introduction of banana mesogens into polymers can result in self-assembled materials in which the molecular dipole correlations are maximized and lead to highly polar structures.

We are interested in developing novel architectures of liquid crystalline polymers containing banana mesogens differently located within the macromolecular structure (Fig 1). These chemical variations may in fact help establish new structure-property correlations and provide guidelines to design special liquid crystalline materials.

In this work we incorporated banana mesogens into the main chain of a completely new class of liquid crystalline polymers via the acyclic diene metathesis (ADMET) polymerization [8,9] of banana monomers. We also prepared another architecture of liquid crystal polymers consisting of a regular alternation of a banana unit and a calamitic unit along the main chain (Fig. 1). The structures of the banana diene monomers used are shown in Figure 2.

FIGURE 1 Schematic of the main-chain polymers prepared with banana units (a), and alternating banana and calamitic units (b).

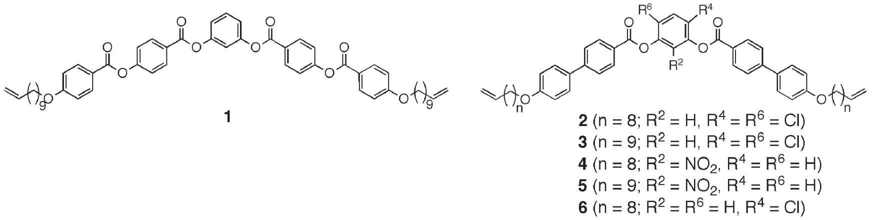


FIGURE 2 Structures of the banana monomers **1–6** used.

EXPERIMENTAL PART

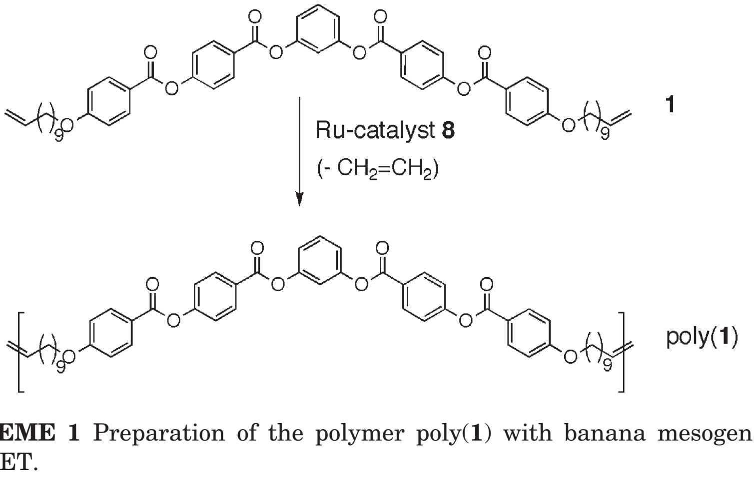
Synthesis

The monomers, 1,3-phenylene bis{4-[4′-(10-undecenyloxy)benzoyloxy]-benzoate} (**1**) [10] and 1,3-phenylene bis{[4′-(alkenyloxy)]-1,1′-biphenyl-4-carboxylate}s ($n = 8$ or 9) **2–6** [11], were synthesized according to literature procedures.

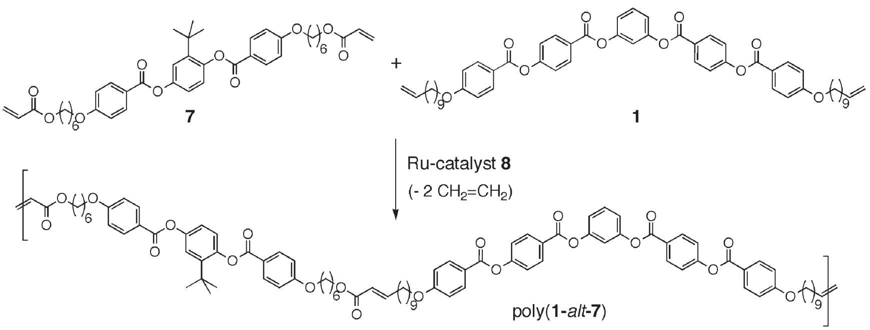
The ruthenium catalyst **8**, (tricyclohexylphosphine)(1,3-dimesitylimidazolidine-2-ylidene)benzylideneruthenium dichloride, was used as received from Aldrich.

Examples of ADMET polymerizations are given below for the homopolymerization of **1** (Scheme 1) and the copolymerization of **1** with **7** (Scheme 2).

Poly(**1**): A Schlenk-tube was charged with monomer **1** (100 mg, 0.112 mmol) and catalyst **8** (1 mg, 0.0012 mmol) dissolved in degassed 1,2-dichloroethane (0.5 mL) was added under inert atmosphere. The



SCHEME 1 Preparation of the polymer poly(**1**) with banana mesogens by ADMET.



SCHEME 2 Preparation of the alternating copolymer poly(**1**-*alt*-**7**) with both banana and calamitic mesogens.

reaction mixture was heated to 55°C for 1 h. During that time, gaseous components were removed every 20 min by pump-flush cycles. The reaction mixture was then evaporated to dryness and heated for an additional 15 min to 55°C applying full vacuum (0.01 mbar). The residue was dissolved in CH_2Cl_2 (3 mL) and excess ethyl vinyl ether (100 μL) was added to deactivate the catalyst. The reaction mixture was stirred for 10 min at ambient temperature and then slowly poured into stirred methanol at 0°C. The precipitate was filtered, purified by repeated precipitations from CH_2Cl_2 solutions into methanol at 0°C and dried under vacuum. Yield 87%.

^{1}H-NMR (δ 500 MHz, 20°C, $CDCl_3$): 8.29 (d, 4H, $Ph^{2',6'}$), 8.16 (d, 4H, $Ph^{2'',6''}$), 7.51 (t, 1H, Ph^5), 7.39 (d, 4H, $Ph^{3',5'}$), 7.22 (m, 3H, $Ph^{2,4,6}$), 7.00 (d, 4H, $Ph^{3'',5''}$), 5.41 (m, 2H, CH=CH), 4.06 (t, $J = 7$ Hz, 4H, OCH_2), 2.02 (m, 4H, $C\underline{H}_2CH{=}CH$), 1.84 (m, 4H, $C\underline{H}_2CH_2O$), 1.5–1.3 (m, 24H, CH_2).

$^{13}C\{^1H\}$-NMR (δ 125 MHz, 20°C, $CDCl_3$): 164.6, 164.4, 164.1 (4C, C=O, $Ph^{4''}$), 155.7 (2C, $Ph^{4'}$), 151.7 (2C, $Ph^{1,3}$), 132.7, 132.1 (8C, $Ph^{2',6',2'',6''}$), 130.6 (2C, CH=CH), 130.2 (1C, Ph^5), 126.9 (2C, $Ph^{1'}$), 122.4 (4C, $Ph^{3',5'}$), 121.2 (1C, $Ph^{1''}$), 119.6 (2C, $Ph^{4,6}$), 116.1 (1C, Ph^2), 114.7 (4C, $Ph^{3'',5''}$), 68.6 (2C, OCH_2), 32.9 (2C, $\underline{C}H_2CH{=}CH$), 29.9–26.2 (14C, CH_2).

FT-IR (NaCl, cm^{-1}): 2924 (m), 2853 (w), 1736 (s, νC=O), 1603 (s), 1510 (m), 1474 (w), 1413 (w), 1310 (w), 1255 (s), 1207 (m), 1161 (s), 1131 (s), 1058 (s), 1015 (m), 910 (w), 888 (w), 845 (m), 801 (w), 762 (m), 689 (w), 667 (w).

Poly(**1**-*alt*-**7**): A Schlenk-tube was charged with monomer **1** (0.055 mmol) and monomer **7** (0.055 mmol) and catalyst **8** (0.0012 mmol) dissolved in degassed dichloromethane (0.5 mL) was added under inert atmosphere. The reaction mixture was heated to 45°C for 4 h. The reaction mixture was then evaporated to dryness, the residue was dissolved in CH_2Cl_2 (3 mL) and excess ethyl vinyl ether (100 μL) was added to deactivate the catalyst. The reaction mixture was stirred for 10 min at ambient temperature and then slowly poured into stirred methanol at 0°C. The precipitate was filtered, purified by repeated precipitations from CH_2Cl_2 solutions into methanol at 0°C and dried under vacuum. Yield 92%.

^{1}H-NMR (δ 500 MHz, 20°C, $CDCl_3$): 8.29 (d, 4H, $Ph^{A2',6'}$), 8.17 (m, 8H, $Ph^{A2'',6''}$, $Ph^{B2',6'}$), 7.51 (t, 1 H, Ph^{A5}), 7.39 (d, 4H, $Ph^{A3',5'}$), 7.25 (d, $J =$ 2 Hz, 1 H, Ph^{B3}), 7.22 (m, 3 H, $Ph^{A2,4,6}$), 7.13 (m, 2 H, $Ph^{B5,6}$), 7.00 (m, 10 H, $Ph^{A3'',5''}$, $Ph^{B3',5'}$, $OCCH{=}C\underline{H}$), 5.84 (d, $J = 16.0$ Hz, 2 H, $OCC\underline{H}{=}CH$), 4.15 (t, $J = 7$ Hz, 4 H, $OCOCH_2{}^B$), 4.06 (m, 8 H, OCH_2), 2.21 (m, 4 H, $C\underline{H}_2CH{=}CH$), 1.38 (s, 9 H, CH_3), 1.9–1.2 (m, 44 H, CH_2).

$^{13}C\{^1H\}$-NMR (δ 125 MHz, 20°C, $CDCl_3$): 167.1, 165.3, 165.2, 164.6, 164.4, 164.1, 163.9, 163.8, 163.7 (12C, C=O, $Ph^{A4''}$, $Ph^{B4'}$), 155.7 (2C, $Ph^{A4'}$), 151.7 (2C, $Ph^{A1,3}$), 149.8 (2C, $OCCH{=}\underline{C}H$), 148.4 (1C, Ph^{B4}), 147.1, 147.0 (1C, Ph^{B1}), 143.1 (1C, Ph^{B2}), 137.8 (1C, Ph^2-A), 132.7, 132.6, 132.5, 132.1 (12C, $Ph^{A2',6',2'',6''}$, $Ph^{B2',6'}$), 130.2 (1C, Ph^{A5}), 126.9 (2C, $Ph^{A1'}$), 125.3 (1C, Ph^{B6}), 122.4 (4C, $Ph^{A3',5'}$), 122.0, 121.9 (2C, $Ph^{B1'}$), 121.4 (2C, $OC\underline{C}H{=}CH$), 121.2 (1C, $Ph^{A1''}$), 120.8, 120.3 (2C, $Ph^{B3,5}$), 119.6 (2C, $Ph^{A4,6}$), 114.7, 114.5 (8C, $Ph^{A3'',5''}$, $Ph^{B3',5'}$), 68.4 (4C, $PhOCH_2{}^{A,B}$), 64.4 (4C, $OCOCH_2{}^B$), 34.9 (1C, $C(CH_3)_3$), 32.5 (2C, $\underline{C}H_2CH{=}CH$), 30.4 (3C, CH_3), 29.7–26.0 (22C, CH_2).

FT-IR (NaCl, cm^{-1}): 2929, 2855 (m), 1734 (s, νC=O), 1654 (w), 1604 (s), 1579 (w), 1510 (m), 1484 (w), 1421 (w), 1392 (w), 1314 (w), 1253 (s), 1206 (m), 1160 (s), 1128 (m), 1056 (m), 1015 (m), 1007 (m), 912 (m), 845 (w), 804 (w), 762 (m), 733 (m), 691 (w), 646 (w), 629 (w).

Characterization

NMR (^{1}H, ^{13}C) spectra were recorded on a Varian INOVA 500 MHz spectrometer and referenced to $SiMe_4$. The relaxation delay was set to 10 s for ^{1}H-NMR spectra and to 2 s for $^{13}C\{^1H\}$-spectra.

The number and weight average molecular weights (M_n, M_w) and the polydispersity index (M_w/M_n) were determined by size exclusion chromatography (SEC) with THF as the solvent using the following arrangement: Merck Hitachi L6000 pump, separation columns from Polymer Standards Service, 8 × 300 mm STV 5 μm grade size (10^6 Å, 10^4 Å, and 10^3 Å), refractive index detector from Wyatt Technology, model Optilab DSP interferometric refractometer. Polystyrene standards (from Polymer Standard Service) were used for calibration.

Differential scanning calorimetry (DSC) measurements were performed with a Mettler DSC-30 instrument (10°C·min^{-1}). The phase transition temperatures were taken as the maximum temperature in the DSC enthalpic peaks. The glass transition temperature was set at the half-devitrification temperature.

The X-ray diffraction experiments were performed on powder-like samples with a Guinier camera as well as a Guinier goniometer using the Cu-Kα radiation ($\lambda = 1.54$ Å).

RESULTS AND DISCUSSION

A vast majority of banana liquid crystals contain five interconnected aromatic rings, the overall bent shape mainly deriving from a central *meta* phenyl core [3]. Several chemical variations of the basic structure have been explored, including the introduction of diverse linking groups between the aromatic rings that can additionally carry lateral substituents [12]. Terminal flexible tails are also helpful in promoting the onset of banana phases at relatively low temperatures.

In our special variation we used alkenyl chains of varied lengths ($n = 8$ or 9) as terminal groups of diene banana monomers (Fig. 2). The C=C double bonds of the vinyl groups could in fact be exploited to create new structures of liquid crystal polymers incorporating main-chain banana mesogens (Fig. 1a). In one further variation, rod-like mesogens from calamitic monomers could also be combined in the same structure of main-chain polymers (Fig. 1b).

The length of the alkenyl terminal tails slightly affected the mesophase behavior of the banana monomers, which was primarily dictated by the nature of the bent-shaped core, see **2** and **3** or **4** and **5** (Table 1). While chlorine groups in the 4-position or 4,6-positions of the central

TABLE 1 Mesophase Behavior of the Banana Monomers **1–6** and Calamitic Monomer **7**

Monomer	R^2	R^4	R^6	n	Phase transitions (in °C)^a
1	H	H	H	9	Cr 101 (B_2 98) I
2	H	Cl	Cl	8	Cr 88 N 99 I
3	H	Cl	Cl	9	Cr 79 N 103 I
4	NO_2	H	H	8	Cr 119 (B_7 113) I
5	NO_2	H	H	9	Cr 110 B_7 118 I
6	H	Cl	H	9	Cr 90 (N 82) I
7	–	–	–	6	Cr 59 (N 46) I

[a] By DSC and optical microscopy. Monotropic phases in parentheses.

phenyl ring favored the formation of a nematic phase, the nitro group in the 2-position promoted the occurrence of a B_7 phase. These appear to be rather general features for banana mesogens [3,13]. Monomer **1** exhibited a monotropic B_2 phase. Such a mesophase is certainly one among the most interesting B phases because of its switching characteristics under an applied electric field [3,14]. Details of the mesophase behavior and physical properties were discussed elsewhere [10,11].

Diacrylate **7** is a conventional calamitic monomer that exhibited a monotropic nematic phase (Scheme 2). The introduction of a bulky *t*-butyl group on the central *para* phenyl ring lowers the clearing temperature to close to ambient.

The monomers were polymerized by ADMET in the presence of the ruthenium catalyst **8** ([monomer]/[catalyst] = 100:1 initial ratio) to give the corresponding polymers with liberation of ethylene (Scheme 1). To achieve high yields it was necessary to remove the gaseous by-product from the reaction medium. The metathesis reaction was quenched conventionally by adding ethyl vinyl ether at room temperature after 1–2 h polymerization time. Longer reaction times than 2 h did not lead to polymers with higher molecular weights. This is presumably because of increasing "back-biting" of the initiator, which results in degradation of the formed polymer and production of cyclic oligomers.

The well-defined ruthenium carbene complex **8** [15] (Fig. 3) is a highly active catalyst in a variety of olefin metathesis reactions, and additionally is highly tolerant of polar and protic functional groups in the monomers [15–17]. This feature also permitted us to prepare functional polymers with polar groups, such as poly(**2**) through poly(**6**).

Although ADMET is similar to ring-opening metathesis polymerization (ROMP) [18], it is mechanistically different because in each propagation step, the polymer chain is ejected from the active metal species, making ADMET a step-like condensation polymerization [16]. In general, ADMET polymerizations are less active and yield less defined polymers than the chain-growth ROMP method. Consistent

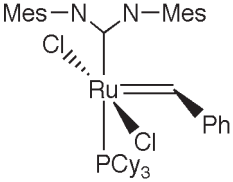


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FIGURE 3 The ruthenium catalyst used for the ADMET polymerizations.

TABLE 2 Physico-chemical Characteristics of the ADMET Polymers Prepared

Polymer	Reaction time[a] (h)	Yield (%)	M_w^b (g·mol^{-1})	M_w/M_n^b
poly(**1**)	1	87	22000	2.1
poly(**2**)	1	93	24800	1.9
poly(**3**)	2	83	44300	1.7
poly(**4**)	2	89	33700	2.2
poly(**5**)	1	86	16700	1.7
poly(**6**)	1	85	16500	1.9
poly(**1**-*alt*-**7**)	4[c]	92	49100	1.8

[a] At 55°C, unless specified otherwise.
[b] By SEC with polystyrene standards.
[c] At 45°C.

with this interpretation, polymers with relatively high molecular weight and narrow molecular weight dispersity were obtained (Table 2). The *cis*/*trans* ratio of the formed double bond along the polymer backbone was about 20/80.

Furthermore, reaction of a 1:1 mixture of monomers **1** (diene, A) and **7** (diacrylate, B) with catalyst **8** gave the corresponding A–B alternating copolymer poly(**1**-*alt*-**7**) in high yields (Scheme 2). A degree of alternation of 96% was determined by ^{1}H-NMR spectroscopy following a literature method [17]. Thus, an almost perfect alternation of calamitic and banana mesogens along the polymer main chain was obtained, which in turn were separated by long and flexible spacers.

The proposed mechanism for such alternating ADMET polymerization, named ALTMET [6], is believed to be quite similar to ring-opening insertion metathesis polymerization (ROIMP) [17]: In a first stage, the ADMET polymer was formed from the diene monomer **1**, and later on in a second stage the diacrylate units **7** were incorporated into the polymer backbone. However, in contrast to ADMET, ALTMET did not require the use of high vacuum and elevated temperatures to reach completeness of the reaction and to yield high molecular weight polymers. This finding is explained by the irreversibility of the insertion reaction of the acrylate group on the main-chain C=C double bond in the latter system. Moreover, the configuration of resulting olefin double bond in the polymer chain was only *trans*, within the NMR detection limits.

Some of the polymers prepared exhibited a thermotropic mesophase behavior. While polarizing optical microscopy observations confirmed the occurrence of liquid crystal phases, they did not evidence characteristic textures. This fact is normal for polymers in which the polydomain nature of the viscous melt prevents typical optical textures to evolve.

We started a more detailed investigation of the mesophase behavior by DSC and X-ray diffraction studies. Homopolymers poly(**1**), poly(**3**), poly(**5**), poly(**6**), each based on a different mesogen, and copolymer poly(**1**-*alt*-**7**) were selected as representative examples of their structural classes. Poly(**3**) and poly(**6**) formed a persistent nematic phase up to the respective clearing temperatures of 161°C and 130°C. Their glass transition temperature was relatively high (59°C and 73°C, respectively), and therefore the nematic phase remained frozen in the glassy state at room temperature. By contrast, poly(**5**) was semicrystalline with a high melting temperature at 158°C, which in fact inhibited the onset of mesomorphism. In poly(**1**) the mesophase extended from the clearing temperature (151°C) across the glass temperature (68°C) down to room temperature. The X-ray diagrams present a set of four reflections in the small angle region (Fig. 4) together with a diffuse halo around a Bragg angle of 10°. This points to a columnar structure, but the impossibility to orient the samples prevented the evaluation of the pattern on the basis of a definite two-dimensional lattice. Nevertheless, it is worth noting that a bent-shaped monomer able to form a banana mesophase can give rise to a columnar mesophase, when inserted as a constituent into a polymer main chain.

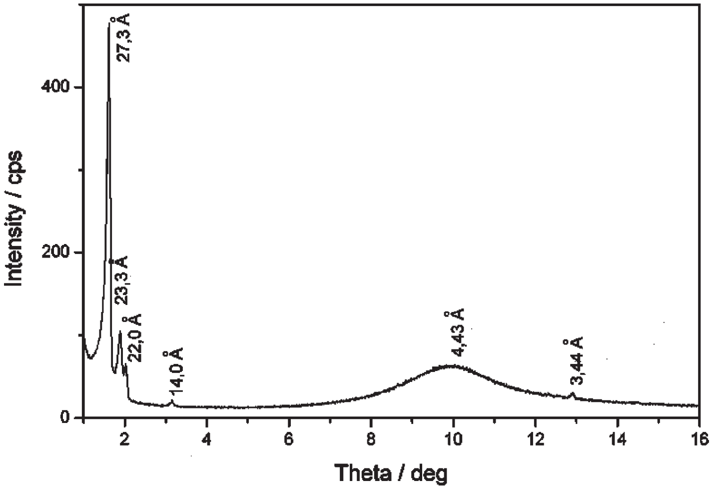

FIGURE 4 X-ray diffraction pattern of poly(**1**) at 120°C.

Copolymer poly(**1**-*alt*-**7**) formed a nematic phase between the glass temperature at 39°C and the clearing temperature at 93°C. In this particular case, combination of banana with calamitic units along the macromolecular chain results in a nematic phase that may have peculiar characteristics. Indeed, the microscopic structure and the macroscopic properties of the nematic phase of banana mesogens have not been studied in detail so far, as opposed to the classical nematic phase of calamitic molecules. It is also pertinent to remind here that banana molecules and calamitic molecules are largely mutually immiscible and their binary mixtures typically macrophase separate over broad ranges of composition [19]. Connectivity of such immiscible mesogens along a polymer chain makes it impossible for them to separate macroscopically and would possibly provide a means to tune their phase behavior and properties. One other structural variant containing banana and calamitic mesogenic units has been recently realized by the synthesis of macrocyclic molecules [20]. In that case, the simultaneous presence of both types of units in the same molecular architecture seemed essential for the formation of liquid crystalline phases.

CONCLUSIONS

We have presented novel macromolecular architectures of ADMET polymers comprising banana mesogens in the main chain. This technique is versatile and also permits chemical variations to be performed. In fact, the possibility of combining banana mesogens and calamitic mesogens in one polymer structure can significantly enlarge the scope of ADMET in liquid crystal science.

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