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Liquid crystal formation of multibranched polystyrene induced by molecular anisotropy associated with its high branch density

Yasuhisa Tsukahara*, Yoshinori Ohta and Kazunobu Senoo
Department of Materials Science, Kyoto Institute of Technology, Matsugasaki, Kyoto 606, Japan
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Polarization microscopic observation was carried out for solvent-cast films and solutions of multibranched polystyrenes. The multibranched polystyrenes were prepared by the radical polymerization of ω-methacryloyloxyethyl polystyrene macromonomers of different molecular weights. It was found that multibranched polystyrene, with long flexible polystyrene chains and without any mesogenic groups, form the mesomorphic phase depending on the branching architecture of the polymer molecule. The formation of the liquid crystalline phase indicates that the multibranched polystyrenes possessing large branch number and sufficient branch length behave as rod-like molecules. The large molecular anisotropy might be caused by the stretching of the backbone chain to maximize the conformational entropy of the individual flexible branch chains. The cast films of the multibranched polystyrene/linear polystyrene blend (50/50 by weight) showed the phase-separated structure of the mesomorphic domains dispersed in the isotropic matrix.

(Keywords: liquid crystal; mesophase; polystyrene macromonomer)

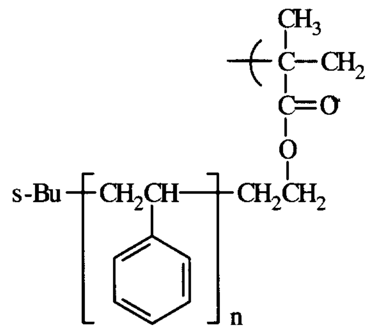
Introduction

Anisotropic molecules having a large axial ratio, such as rod-like or disc-shaped small molecules, form a liquid crystalline phase or mesomorphic phase under suitable conditions. Ever since discovery of the liquid crystalline phase by Lehmann and Reinitzer, many compounds forming the liquid crystalline phase have been synthesized. Polymer molecules having a stiff main chain or a flexible main chain with mesogenic side groups are also known to form the mesomorphic phase as main-chain type[1,2] or side-chain type[3] liquid crystalline polymers. Liquid crystalline compounds and resulting mesomorphic phases are now known to play a very essential part in diverse fields, from cell membranes in living tissues to electronic displays, sensors and holography[4].

In this report, we demonstrate an experimental discovery that multibranched polystyrene, with long flexible polystyrene chains and without any mesogenic groups, forms the mesomorphic phase depending on the branching architecture of the polymer molecule.

Experimental

Multibranched polystyrenes are poly(macromonomer)s, i.e. polymerization products of polystyrene macromonomers having a methacryloyloxyethyl group at the ω-chain end. The macromonomers of different molecular weights were synthesized by the living anionic polymerization technique[5,6]. These macromonomers were polymerized using azobisisobutyronitrile as an initiator in benzene at 60°C for 24 h. Polymerization products were purified by precipitation–extraction procedures with cyclohexane–petroleum ether mixed solvents to isolate the poly(macromonomer), the chemical structure of which is:



Poly(MA-PSt)s

Molecular characteristics of the multibranched polystyrenes are summarized in *Table 1*. Values of M_w and M_w/M_n were determined by gel permeation chromatography (g.p.c.) (Tosoh HLC802A) equipped with a low-angle laser light scattering detector (Tosoh LS-8) and a refractive index detector[5].

Polarization microscopic observation of the cast films of poly(macromonomer)s and the blend with linear polystyrene ($M_n = 10.3 \times 10^4$, $M_w/M_n = 1.02$) were carried out using a Nikon Optiphot2-Pol at room temperature (20°C) under crossed Nicols. Both the poly(macromonomer)s and the blends were cast from xylene or toluene solution (10 wt%) onto glass slides in a covered laboratory dish at room temperature (20°C). After evaporation of the solvent, the film specimens were directly observed and polarized light microphotographs were taken. Toluene solutions of known concentrations were prepared in a glass sample tube of 1 cm diameter and the microphotographs were taken from the outside.

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* To whom correspondence should be addressed

Table 1 Molecular characteristics of multibranched polystyrenes

Sample code[a]	$M_w \times 10^{-4}$[b]	M_w/M_n	k[c]	n[d]	Observation of mesophase
Poly(MA-PSt2900)	316	1.18	1019	26.3	yes
	150	1.78	484	26.3	yes
	139	2.77	448	26.3	yes
	6.3	1.86	20	26.3	no
Poly(MA-PSt800)	154	2.00	1730	6.1	no
	48.9	2.13	549	6.1	no

[a] The numerals in the sample code of poly(macromonomer)s represent the number-average molecular weight (M_n) of the macromonomer
[b] Determined by g.p.c. using a low-angle light scattering detector
[c] Number of branch chains
[d] Number of styrene units per polystyrene branch

Results and discussion

The polystyrene macromonomers were synthesized by living anionic polymerization with s-BuLi. Thus, the polystyrene branches of poly(macromonomer)s have an amorphous nature because of atactic chain structure and uniform molecular weights. In addition, every repeating unit in the backbone chain of the poly(macromonomer)s possesses one polystyrene branch at all times, thus the branch period is also regular and the branch density is extremely high[7–11]. Preparation of such multibranched polymers is very difficult to achieve by the conventional coupling method.

Figure 1 shows polymerization microphotographs taken for the toluene solution of poly(MA-PSt2900)s having 484 branches (at polymer volume fraction $V = 0.257$) (*Figure 1a*), and 1017 branches (at $V = 0.122$) (*Figure 1b*) in sample tubes. Bright anisotropic textures are seen in the photographs. The sample solution was transparent and was able to flow gradually in the sample cell.

When the toluene solution of *Figure 1a* was diluted to $V = 0.227$, the anisotropic texture disappeared completely and the microscopic image became dark. This indicates that the volume fraction for the anisotropic–isotropic threshold exists in the range $V = 0.227$–0.257. In fact, coexistence of the anisotropic phase with thin fine texture and isotropic phase was observed at $V = 0.252$.

Recently, we have found[12,13] that the Kuhn's statistical segment length, β, of the central backbone chain is very long for the poly(MA-PSt2900)s with a large degree of polymerization in *Table 1*. The values of β and the molecular diameter, d, were estimated as $\beta = 100$ nm and $d = 10$ nm, using the worm-like chain model by fitting the experimental hydrodynamic radius–molecular weight relationship data[12]. This suggested that the poly(macromonomer)s with a large degree of polymerization behave as rod-like polymers in solution. The formation of the liquid crystalline phase found in this study might directly indicate the rod-like character of the poly(macromonomer).

The volume fraction for the anisotropic–isotropic threshold, V_c, in the rod-like polymer solution has been discussed by Flory's lattice theory[14], Onsager's theory of the second virial approximation[15], and Cotter's treatment with the scaled particle theory[16]. Sato and Teramoto discuss the effect of semiflexibility[17]. Therefore,

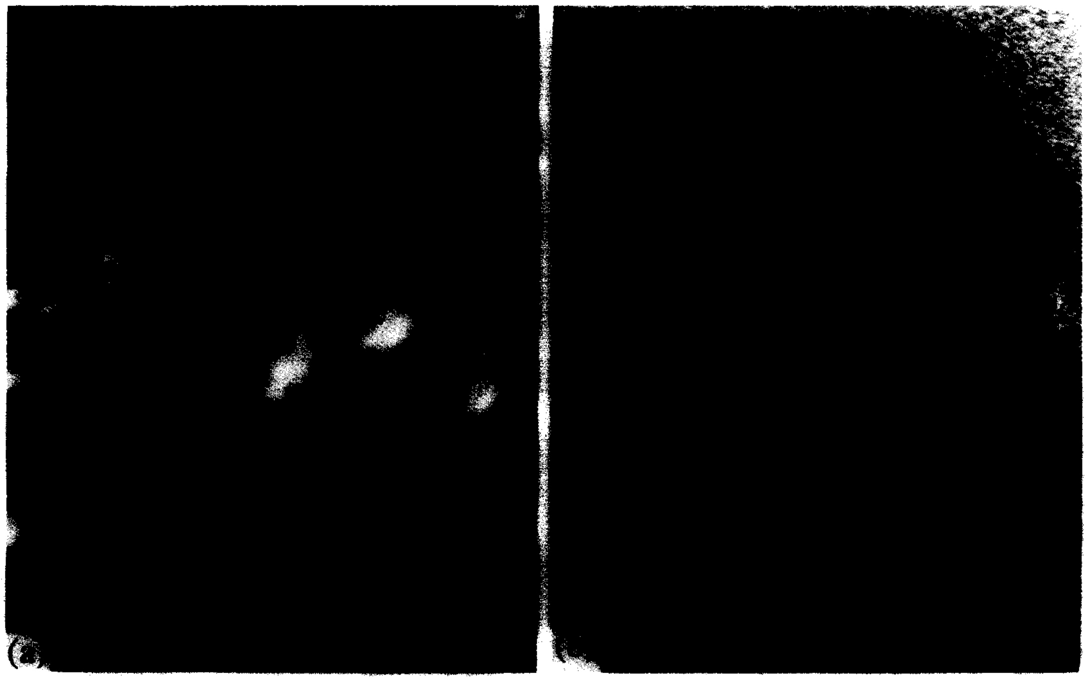

Figure 1 Polarization microphotographs of toluene solutions of poly(MA-PSt2900)s having (a) 484 branches at $V = 0.257$ and (b) 1017 branches at $V = 0.122$. The microphotograph was taken from outside the glass tube at room temperature (20°C) under crossed Nicols. 100× magnification

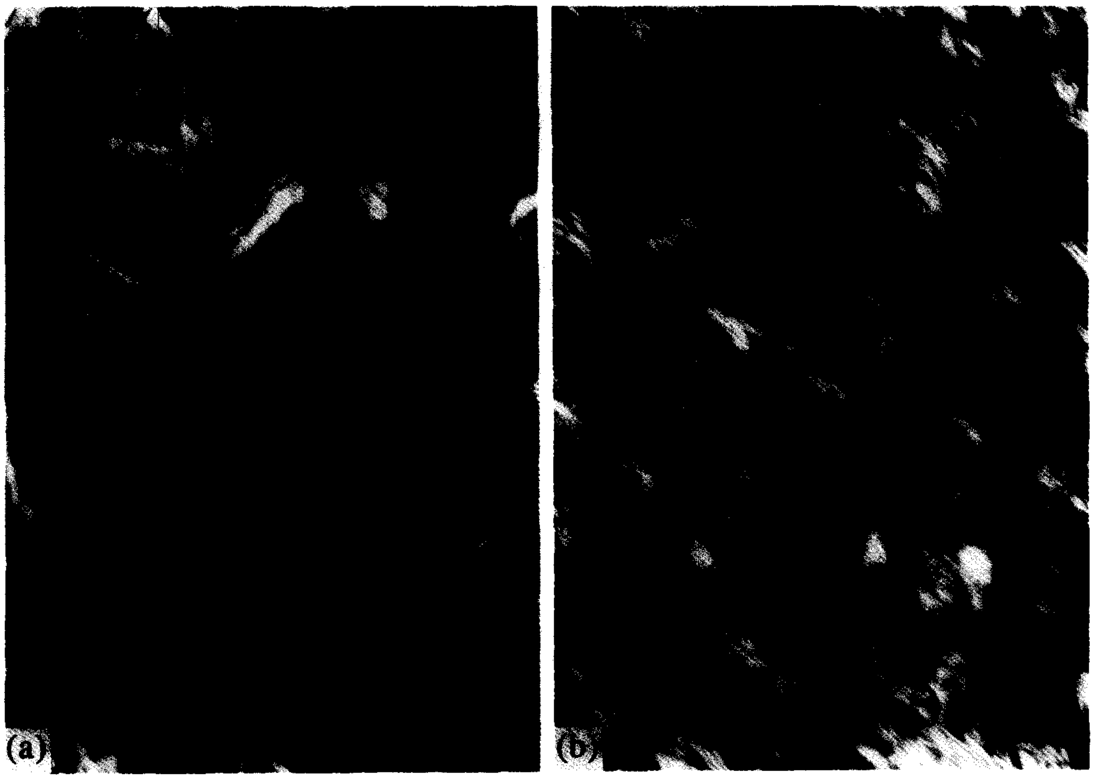

Figure 2 Polarization microphotographs of solvent-cast film specimens of poly(MA-PSt2900) having 448 polystyrene branches cast from xylene solution (10% w/v) at room temperature (20°C). (a) Central region and (b) near-edge region of the cast film specimen. The photographs were taken with 400× magnification at room temperature (20°C) under crossed Nicols. Film thickness is *c.* 0.2 mm

it is very interesting to study the V_c values of the poly(macromonomer)s as functions of the branch number and length. A scattering maximum was observed in the small angle X-ray scattering from the concentrated solution of a poly(macromonomer)[18].

In contrast to the poly(macromonomer)s in *Figure 1*, neither poly(MA-PSt2900) having 20 branches, i.e. a small branch number, nor poly(MA-PSt800) with 1730 branches, but with very short branch length, showed any anisotropic texture at larger V and even in the bulk state. The absence of the anisotropic texture in the poly(MA-PSt800) with 1730 branches is presumably because the branch chain length is not long enough to cause stretching of the backbone chain, where the backbone is not rigid enough to form the mesomorphic phase.

Figure 2 shows polarization microscopic photographs of the film specimen of poly(MA-PSt2900) having 448 branches cast from xylene solution at room temperature (20°C). The photographs were taken with 400× magnification under the crossed Nicols. *Figure 2a* was taken near the centre of the cast specimen, while *Figure 2b* was taken near the edge. Clear and bright anisotropic texture with many throne-like structures is seen in both photographs of *Figure 2*. The anisotropic texture orients randomly in the centre, as seen in *Figure 2a*, while high orientation of the thin throne texture can be observed near the edge of the specimen in *Figure 2b*. This orientation might be induced by the difference in the solvent evaporation rate between the edge and centre regions during solvent casting. The fissure seen in the upper left part of *Figure 2a* is a crack created during solvent evaporation.

Almost the same texture is seen for the specimen cast from toluene solution; however, the texture is on a smaller scale than that of *Figure 2a*, probably because of the faster evaporation rate of toluene than xylene. Thus, the texture might be common for the mesomorphic phase of poly(macromonomer)s in bulk. The solvent-cast film specimens were slightly translucent and were very brittle irrespective of the casting solvent, as reported previously[7].

Figure 3 shows the polarization microphotographs taken for the solvent-cast film of poly(MA-PSt2900) having 484 branches/linear polystyrene ($M_n = 10.3 \times 10^4$) (50/50) blend with different magnifications. It is seen that the bright anisotropic liquid crystalline domains are dispersed in the isotropic matrix. The Schlieren-like texture is seen in the liquid crystalline domains in *Figure 3b*. This indicates that the immiscibility between the poly(macromonomer)s having large branch numbers and linear polystyrene observed in the previous paper[9] is accompanied by the effect of the mesomorphic ordering of the branched polymer component. This anisotropic domain disappeared around 135–140°C, when the temperature was increased at a rate of 10°C min^{-1}.

Although further study is needed, it might be concluded that multibranched polystyrenes possessing a very large number of flexible branch chains with high branch density and sufficient branch length do form the mesomorphic liquid crystalline phase. (The mesomorphic phase of poly(macromonomer)s has been confirmed very recently by another research group[18].) This indicates that poly(macromonomer)s having a high degree of polymerization have large molecular anisotropy due to the polystyrene branches tethered around the

Figure 3 Polarization microphotographs of the film specimen of the poly(MA-PSt2900) with 484 branches/linear polystyrene (50/50 by weight) blend cast from toluene solution (10% w/v) at room temperature (20°C). The photographs were taken near the centre of the cast film with (a) 100× and (b) 400× magnification at room temperature (20°C) under crossed Nicols

central backbone chain[20]. Therefore, the increase of intrinsic viscosity [η], at the large M_w region, in the [η]–M_w relationship reported in the previous paper can be ascribed to the increase in the molecular anisotropy with increasing degree of polymerization[8]. These phenomena are expected to be quite general for other multibranched polymers, with no requirement of any mesogenic groups for the formation of the liquid crystalline phase. Therefore, polymerization of macromonomers provides a novel route to create liquid crystalline polymers.

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