Hydroxypropylcellulose Films as Alignment Layers for Liquid Crystals

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ABSTRACT: Homogeneous surface alignment of liquid crystals (5CB) is observed for films formed by coating with aqueous solutions of hydroxypropylcellulose (HPC) for high coating speeds and thin coating thicknesses. On the other hand, for films formed with isotropic ethanol solutions of HPC, 5CB molecules retain the flow-induced alignment created at the formation of the 5CB droplet. The microstructures responsible for the homogeneous surface alignment are not confirmed in the morphological measurement of the film surface with an atomic force microscope, although large grooves corresponding to the banded texture perpendicular to the coating direction exist on the films formed with liquid crystalline solutions of HPC. The possibility of highly oriented HPC molecules in the coating flow is pointed out using the Doi model. These results suggest that the flow-induced anisotropic orientation of HPC molecules is responsible for the homogeneous surface alignment of 5CB.

Introduction

As an alignment layer of liquid crystal displays (LCDs), rubbed polyimide films are widely used. The rubbing is required for surface alignment of LCs because the polyimide film itself (which formed on a glass substrate) has no ability to align LCs. The rubbing process, however, produces dust and static electricity which give rise to serious problems for the manufacturing process of LCDs. Recently, a number of novel alignment layers, which are rubbing-free, have been proposed: polarized light alignment,[1,2] the applications of Langmuir−Blodgett layers,[3,4] polymer films made by pulsed laser ablation,[5] and UV curable polymer films.[6,7]

The mechanism of LC alignment on the rubbed polymer surface has been discussed by many investigators. However, it has not been understood completely. Concerning the alignment mechanism, the surface morphology of alignment layers have been measured with an atomic force microscope (AFM).[5,6,8] Yamaguchi and Sato[6] demonstrated that anisotropic surface morphology increases the anchoring energy of LCs. However, Luo et al.[5] found that the surface of the polymer film made by pulsed laser ablation is flat, even though LCs align on the film. Shannon et al.[9] used a dichroic azo dye/polyimide mixture film as the alignment layer and demonstrated that polarized light alters the surface alignment of liquid crystals. Furthermore, liquid crystals align perpendicular to the rubbing direction on a rubbed polystyrene film.[10] These facts suggest that for the surface alignment of liquid crystals an anisotropic surface morphological structure is not always required.

Liquid crystalline polymers (LCPs) have been utilized as molded materials because a high degree of molecular orientation induced by the flow in polymer processing is maintained until solidification because of the long relaxation time of orientation. Therefore, LCP film with flow-induced molecular orientation may induce the molecular alignment of LCs. Murakami and Fujii[11] investigated rubbed thin films of main-chain and side-chain LCPs with regards to the application of the LCPs to the alignment layer. However, they did not try to utilize the flow-induced molecular orientation of LCPs for the alignment layer.

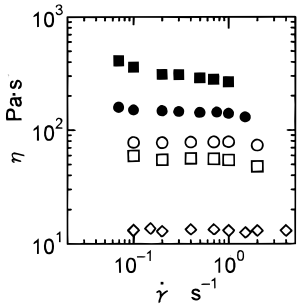

Figure 1. Viscosities of various solutions of HPC: ◇, 20 wt % aqueous solution; ○, 30 wt % aqueous solution; □, 30 wt % ethanol solution; ●, 50 wt % aqueous solution; and ■ 50 wt % ethanol solution.

In the present work, we performed the basic experiments for the application of flow-induced orientation of LCPs to the alignment layer. We examined the effects of coating conditions and polymer concentrations on the surface alignment of liquid crystals, and we observed surface morphology by AFM.

Experimental Section

Film Preparation. Solutions of hydroxypropylcellulose [HPC-L, M_w = 55 000−70 000, supplied by Nippon Soda] were prepared by mixing distilled water or ethanol with HPC at room temperature. Because the critical concentration of aqueous solutions of HPC at the phase transition from an isotropic phase to a liquid crystalline one was about 42 wt %, we used five solutions of HPC: 50 (cholesteric), 30, and 20 wt % (isotropic) aqueous solutions, and 50 (cholesteric) and 30 wt % (isotropic) ethanol solutions. Figure 1 shows the steady shear viscosities of the test solutions.

A glass substrate was coated with the solution of HPC at room temperature and about 70% humidity. The HPC films were cast and sheared by a knife edge moving at a constant speed V which ranged from 0.5 to 5 mm/s. The coating thickness δ, that is the gap between the knife edge and the glass substrate, was adjusted with a micrometer head. The effect of the drying process of the film on the surface alignment

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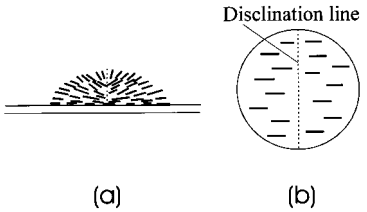


Figure 2. Model of (a) director distribution and (b) disclination line in the NLC droplet for homogeneous surface alignment.

was examined using two kinds of coating thickness of 10 and 40 μm. After the coating, the glass substrate was immediately placed in a desiccator with silica gel, and the coating film was dried for at least 3 days at the room temperature. In the present paper, we will use the following abbreviations for the HPC films: 50-A and 50-E for the films made from the 50 wt % aqueous solution and 50 wt % ethanol solution of HPC, respectively, and so on.

Determination of the Surface Alignment of LCs. Yamaguchi and Sato[12,13] proposed a simple method to determine the alignment of nematic liquid crystals (NLCs): an observation of a droplet of NLC on an alignment surface with a polarizing microscope. If the NLCs uniformly align parallel to the alignment surface, the director of NLCs changes gradually from the parallel alignment at the alignment surface to the perpendicular alignment at the air interface, as shown in Figure 2a. This director distribution causes a straight disclination line perpendicular to the easy axis across the center of the NLC droplet in Figure 2b. On the other hand, when the NLC molecules tilt at the alignment surface, a curved disclination line appears.

We used this method to determine the alignment behavior of NLCs on the LCP film formed by coating. The NLC used in our experiment was 5CB(4-cyano-4′-*n*-pentylbiphenyl). The NLC was carefully dropped from a capillary onto the film surface to form a droplet with the diameter of about 2−3 mm. A long time (more than 1 h) was required for the relaxation of molecular alignment in the droplet. The droplet was observed under a polarizing microscope (Nikon, LABOPHOT2-POL), and the microphotographs of the droplet between crossed polarizers were taken 1 day after the droplet had formed.

Measurement of Surface Morphology. The surface morphology of the HPC films was analyzed using an atomic force microscope (Digital Instruments NanoScope MMAFM-2). The coating direction had been carefully marked on the test sample measured with the AFM before the test sample was cut out of the glass substrate. The AFM measurements were carried out in two scales: 19.4 μm × 19.4 μm and 1 μm × 1 μm.

Results and Discussion

Observation of 5CB Droplets on the HPC Film. Parts a and b of Figure 3 show the microphotographs of the droplet on the 50-A films for the coating thickness $\delta = 10$ μm at the coating speeds $V = 0.5$ and 5 mm/s, respectively. In this range of coating speed, the straight line of disclination clearly is found in the 5CB droplet. The disclination line inclines counterclockwise against the direction perpendicular to the coating direction whenever it is observed; the inclination angle ranges from 15° to 30°. This disclination line indicates that the director of 5CB at the alignment surface uniformly aligns parallel to the alignment surface along the direction perpendicular to the disclination line, as shown in Figure 2. Therefore, the director of 5CB should be at an angle to the coating direction in the plane of the film surface. In the present experiment, however, the reason the disclination line inclines has not been known. Because the 50 wt % aqueous solution of HPC is in the liquid crystalline phase at rest, HPC molecules easily

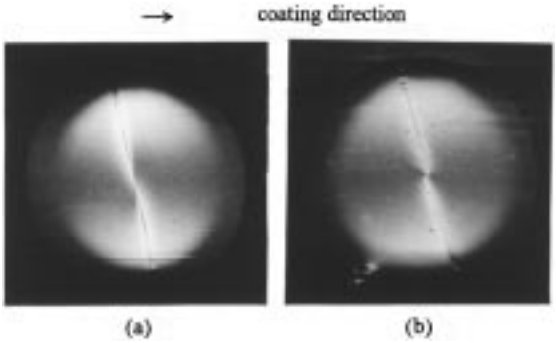


Figure 3. Microphotographs of 5CB droplets on 50-A films for $\delta = 10$ μm. The coating speeds are (a) $V = 0.5$ and (b) $V = 5$ mm/s.

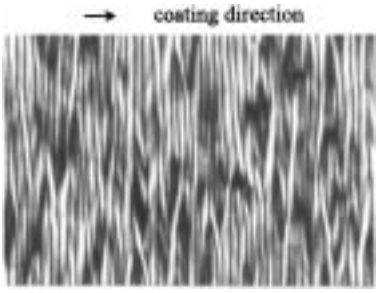


Figure 4. Banded texture in 50-A film formed with $\delta = 10$ μm and $V = 5$ mm/s.

align along the coating direction due to the elongational or shearing flows or both during the coating process. After the flow is stopped, the flow-induced orientation in the solution of LCPs relaxes into an in-plane periodic waving of the director, which causes the banded texture shown in Figure 4. Ernst and Navard[14] found that only a completely anisotropic solution of HPC exhibited the banded texture after stopping the shearing. In the present experiments, the banded texture was observed only in the film made from the 50 wt % solutions at $\delta = 10$ μm. Because the banded texture appears immediately after stopping the shearing under sufficient shear deformations, the in-plane periodic waving of the director seems to be frozen in almost all areas of the film by solidification. Therefore, this anisotropic structure of the molecular orientation of HPC at the film surface is expected to align the 5CB molecules.

The microphotographs of the droplet on the films made from the aqueous solutions of HPC in the isotropic phase are shown in Figure 5. In these films we could not find any texture like the banded one observed through the polarizing microscope. Therefore, almost all areas in these film seem to be isotropic. Despite the isotropic film, the disclination line is clearly observed in the 5CB droplet on the 30-A film as shown in Figure 5a. For the 20-A film, the weak disclination line, which indicates the homogeneous but weak surface alignment of 5CB, exists in the coating condition of $V = 1$ mm/s and $\delta = 10$ μm. A more remarkable disclination line was also obtained at higher speeds of coating for the 20-A film. Thus, it is found that both the concentration of HPC and the coating speed affect the surface alignment of 5CB on the HPC films. Furthermore the surface alignment of 5CB depends on the coating thickness. Parts c and d of Figure 5 show the microphotographs for the thick film ($\delta = 40$ μm). A vague dark cross is observed in the droplet in Figure 5c. The dark cross means that the 5CB molecules align radially on the

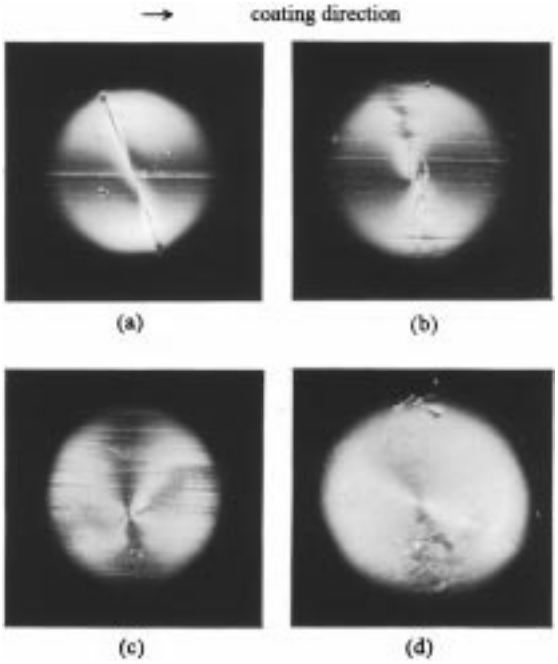


Figure 5. Microphotographs of 5CB droplets on film made from isotropic solutions. The coating conditions are (a) $\delta = 10$ μm and $V = 1$ mm/s for the 30-A film, (b) $\delta = 10$ μm and $V = 1$ mm/s for the 20-A film, (c) $\delta = 40$ μm and $V = 1$ mm/s for the 30-A film, and (d) $\delta = 40$ μm and $V = 5$ mm/s for the 30-A film.

surface of the HPC film because of the flow-induced alignment at the droplet formation. In Figure 5d, neither the disclination line nor the dark cross is observed, although there is an indication of weak homogeneous surface alignment, judging from the change of brightness of the droplet as the microscope table is turned. When we use the mean shear rate $\dot{\gamma}(=V/\delta)$ for the estimate of coating flow, $\dot{\gamma}$ for the film formed at $V = 5$ mm/s and $\delta = 40$ μm equals 120 s^{-1}, and it is larger than 100 s^{-1} at $V = 1$ mm/s and $\delta = 10$ μm. Therefore, not only the flow in the coating process but also the evaporation process of solvent from the film seems to affect the molecular orientation of HPC in the vicinity of the film surface. The results in Figure 5a−d can be interpreted as follows: high coating speeds induces high orientation in general and the flow-induced orientation is fixed in the vicinity of the film surface for the thin film because of fast solidification; however, it relaxes for the thick film because of slow solidification.

Viney and Putnam[15] reported that the formation of the banded texture in HPC solutions is significantly dependent on the solvent type. In our experiment, we also examined the effect of the solvent of HPC solutions on the surface alignment of 5CB. Parts a and b of Figure 6 are the results for the 50-E and 30-E films in the coating conditions of $V = 5$ mm/s and $\delta = 10$ μm, respectively. The banded texture also was observed in the 50-E film. The disclination line is clearly formed in the droplet of 5CB on this film. For the 30-E film, however, the dark cross is found in the droplet of 5CB despite the highest $\dot{\gamma}(= 500\ s^{-1})$, in contrast with the disclination line for the 30-A film shown in Figure 5a. The dark cross in Figure 6b is clearer than that in Figure 5c. This clear dark cross indicates that the flow-induced radial alignment of 5CB molecules remains almost perfectly on the 30-E film because of the random orientation of HPC molecules in the vicinity of the film surface. Because ethanol is a weaker solvent than water,

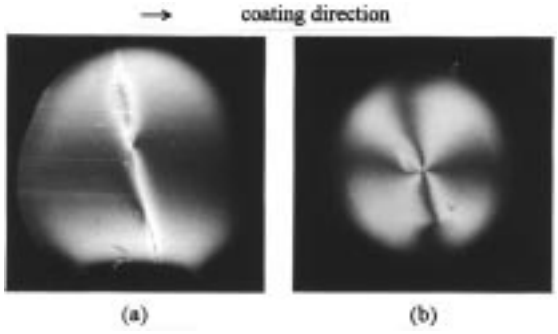
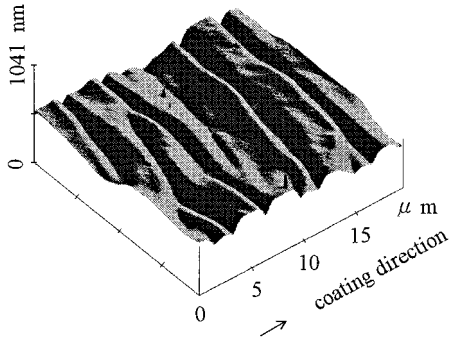
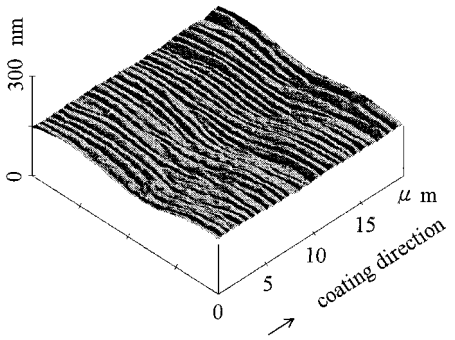


Figure 6. Microphotographs of 5CB droplets on films of (a) 50-E and (b) 30-E. The coating conditions are $\delta = 10$ μm and $V = 5$ mm/s.



(a)



(b)

Figure 7. AFM images of film surface in the scale of 19.4 μm × 19.4 μm. The films of (a) 50-A and (b) 50-E were formed with $\delta = 10$ μm and $V = 5$ mm/s.

it is expected that the polymer chain of HPC in the ethanol solution has a more disordered equilibrium conformation and therefore more probability of entanglement.[15] This entanglement should resist to the flow-induced orientation of HPC molecules and act as the driving force for the relaxation of the molecular orientation. Consequently, coating films formed with isotropic ethanol solutions of HPC have random orientation of HPC molecules, which causes fixation of the flow-induced alignment of 5CB.

Surface Morphology of the HPC Films. Figure 7 shows the surface morphological structures of the 50-A and the 50-E films which have the banded texture. The grooves perpendicular to the coating direction exist in the surface structures of both of the films; these grooves should be associated with the banded texture in the films. The apparent difference between both of the grooves is the groove spacing; it is about 3 μm for the

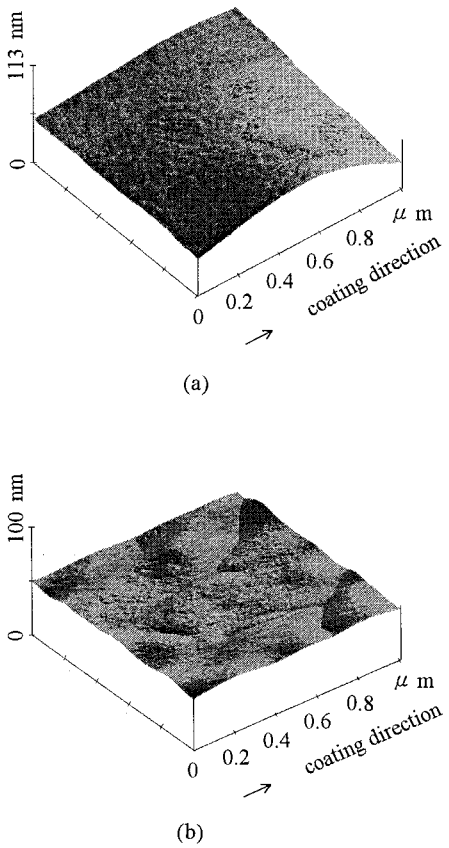


Figure 8. AFM images of film surfaces in the scale of 1 μm $\times$ 1 μm. The films of (a) 50-A and (b) 30-A were formed with $\delta = 10$ μm and $V = 5$ mm/s.

50-A film and about 0.7 μm for the 50-E film. The periodicity of molecular alignment in the banded texture was determined to be about 3.5 μm for both films with the polarizing microscopy. The band spacing changes with time, and its time dependence is affected by the solvent.[15] Therefore, the band spacing at the film surface may be different from that inside the film because the solidification of HPC by drying is faster at the film surface than inside the film. We think that this is one of the reasons for inconsistencies in the groove spacing and the band spacing. Using a low-voltage, high-resolution scanning microscope and an AFM, Patnaik et al.[16] measured the surface morphology of HPC films and observed that the fibrils were sinusoidal about the coating direction with the same wavelength as the shear band: the fibril had an averaged peak-to-valley height of $\approx$120 nm and an average width of $\approx$285 nm. In our HPC film, however, such fibrils have not existed. Their films were cast, sheared, and dried at 85 °C, whereas our HPC films were processed at about 25 °C. Because a long time is required for the drying of the film in our experiment, it may cause the leveling of the fibrillar topology.

We carried out surface morphological measurements on a smaller scale (1 μm $\times$ 1 μm) to check whether smaller anisotropic structures responsible for the homogeneous surface alignment of 5CB exist. Parts a and b of Figure 8 show the AFM images of the 50-A and 30-A films for $V = 5$ mm/s and $\delta = 10$ μm, respectively. The anisotropic structures such as the microgrooves along the rubbing direction seen in rubbed alignment films[6] are not observed in all cases, although the 50-A and 30-A films have a homogeneous surface alignment in this coating condition. From the results of AFM measurements, the anisotropic orientation of HPC molecules at the film surface is considered to be responsible for the homogeneous surface alignment of 5CB.

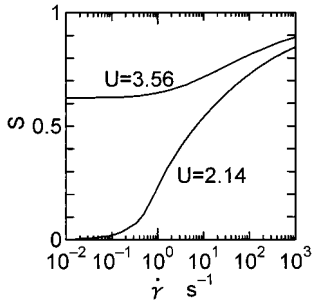


Figure 9. Shear rate dependence of the scalar order parameter.

A Simple Estimate of Molecular Orientation of HPC in the Coating Flow. In our experiment, we obtained a good homogeneous alignment of 5CB on the HPC film for high concentrations of HPC, high coating speeds, and thin coating thicknesses. Therefore, it is apparent that the flow-induced orientation and the relaxation of orientation in the drying process are dominant to the formation of the anisotropic orientation of HPC molecules at the film surface. Because it is hard to analyze the molecular orientation in the real coating process, we use a simple shear flow to estimate the flow-induced orientation of HPC aqueous solutions in the coating flows. The constitutive equation used is the Doi model[17] for the concentrated solution of rigid rodlike molecules. The orientation of the rods in the Doi model is described by an orientational order-parameter tensor S_{ij}, defined by

$$S_{ij} = \langle u_i u_i, - {}^1/_3 \delta_{ij} \rangle \tag{1}$$

where u_i is a unit vector specifying the rod orientation and $\langle \cdots \rangle$ denotes an average over the distribution function. The kinetic equation for the orientational order-parameter tensor is given by

$$\frac{\mathrm{D}S_{ij}}{\mathrm{D}t} = F_{ij}(\mathbf{S}) + G_{ij}(\mathbf{S}) \tag{2}$$

where

$$F_{ij}(\mathbf{S}) = -6\overline{D_r}\left[\left(1 - \frac{U}{3}\right)S_{ij} - U(S_{ik}S_{jk} - {}^1/_3\delta_{ij}S_{kl}{}^2) + US_{ij}S_{kl}{}^2\right] \tag{3}$$

$$G_{ij}(\mathbf{S}) = {}^1/_3(v_{i,j} + v_{j,i}) + v_{i,k}S_{kj} + v_{j,k}S_{ki} - {}^2/_3\delta_{ij}v_{k,l}S_{kl} - 2v_{k,l}S_{kl}S_{ij} \tag{4}$$

Here, v_i is the velocity vector, U the dimensionless parameter proportional to the concentration ν, and $\overline{D_r}$ the rotational diffusivity. Doi approximated $\overline{D_r}$ by

$$\overline{D_r} = D_r(1 - {}^3/_2 S_{ij}{}^2)^{-2} \tag{5}$$

where D_r is the rotational diffusivity in the isotropic solution proportional to ν^{-2}. The values of the parameters used are $D_r = 0.6$ s^{-1} and $U = 3.56$ for the 50 wt % aqueous solution of HPC[18] and $D_r = 1.67$ s^{-1} and $U = 2.14$ for the 30 wt % aqueous solution of HPC.

Figure 9 shows the shear rate dependence of scalar order parameter S for the 50 and the 30 wt % aqueous solutions of HPC. The scalar order parameter is given by

$$S = ({}^3/_2 S_{ij}{}^2)^{1/2} \tag{6}$$

The scalar order parameter for the 30 wt % aqueous solution rapidly increases beyond the shear rate of 0.5 s^{-1} and exceeds the equilibrium value of 50 wt % aqueous solution at $\dot{\gamma} \cong 30$. Because the coating process was carried out at the shear rates ranging from 12.5 to 500 s^{-1} in our experiments, the comparatively high orientation of HPC molecules seems to be induced by the coating flow even for the 30 wt % aqueous solution. Mori et al.[19] demonstrated the occurrence of high orientation of molecules due to the elongational flow near the filament surface at the nozzle lip in the numerical simulation of a spinning flow of liquid crystalline polymers using the Doi model. Therefore, the high orientation of HPC molecules due to the elongational flow is also expected particularly in the vicinity of the film surface at the knife edge in our experiment. From this consideration, we think that the anisotropic alignment of HPC molecules, which causes the homogeneous surface alignment of 5CB, remains in the vicinity of the surface of the 30-A film.

Conclusion

In our experiment, we found the homogeneous surface alignment of 5CB on the HPC films for high concentrations of HPC, high coating speeds, and thin coating thicknesses. The morphological measurement of the film surface with the AFM provided no evidence of the existence of the anisotropic surface structures. Therefore, the homogeneous surface alignment of 5CB can be explained by the flow-induced orientation of HPC molecules fixed in the vicinity of the film surface. Moreover, the estimate of scalar order parameter in the simple shear flow using the Doi model supports this idea, although the effect of the drying process on the molecular orientation in the HPC films is still unknown.

Our novel idea for the alignment layer of liquid crystals is to utilize the property of LCPs that a high degree of orientation is easily obtained by the flow and maintained until solidification because of the long relaxation time of orientation. Therefore, it may be possible to use a polymer other than the HPC-L used in our experiment, if it has this property.

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