Materials Science-Poland, Vol. 22, No. 4, 2004

Zone casting – a universal method of preparing oriented anisotropic layers of organic materials

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A method for the preparation of oriented, anisotropic layers of soluble molecular materials on substrates that were not pre-oriented (so-called zone casting) is presented. The method consists in casting a suitable solution, continuously supplied by a nozzle, onto a moving substrate. Solvent evaporation takes place from the surface of the meniscus formed between a special flat nozzle and the substrate. Due to a gradient of the solute concentration, its solidification proceeds in a narrow zone under highly anisotropic conditions. The conditions of stationary deposition and the influence of various parameters on the process, such as casting speed, the diffusion coefficient, evaporation rate, are discussed. It is shown that the zone casting can be used to obtain anisotropic layers of many different low-molecular-weight and macromolecular materials.

Key words: *zone casting; solution processing; orientation; anisotropy*

1. Introduction

Physical properties of organic molecules exhibiting interesting electrical and optical properties are usually highly anisotropic. Therefore, the preparation of materials in which molecules are appropriately arranged is of a great importance. Obtaining sufficiently large single crystals is usually very difficult or impossible. Anisotropic layers of organic materials of distinctive properties in the direction perpendicular to the substrate surface can be obtained by some methods, e.g. by the Langmuir–Blodgett technique or, to some extent, by vacuum deposition. It is more difficult to achieve good orientation in the direction parallel to the substrate, which can be obtained by mechanical deformation or by solution casting on pre-oriented substrates. In this communication, we present an alternative method of preparing oriented anisotropic layers

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of molecular materials (which can be solution-processed) on substrates not having been pre-oriented. The conditions of stationary deposition in the zone casting method, developed in the Centre of Molecular and Macromolecular Studies of the Polish Academy of Sciences [1–4], are discussed and examples of applications for different classes of materials are presented.

2. Description of the technique

Zone casting consists in the deposition of a material from solution on a moving substrate. The casting process is schematically presented in Fig. 1.

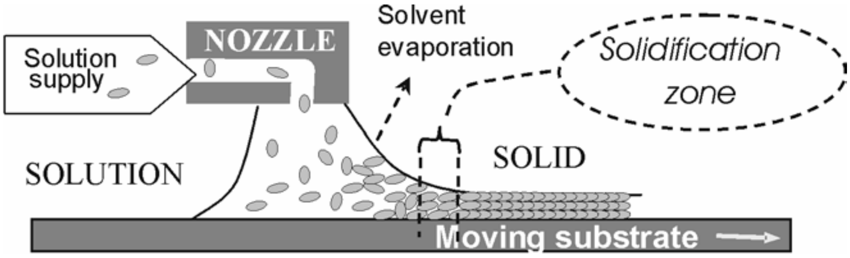

Fig. 1. Schematic presentation of the zone casting technique

The solution is continuously supplied to the evaporation zone by a flat nozzle. The solvent evaporates from the meniscus zone and the solute is deposited on the moving substrate. The solution supply rate, substrate velocity, initial solute concentration, solvent evaporation rate, and crystallisation rate must be chosen properly to obtain stationary conditions. The last two parameters can be controlled by a choice of the solvent and casting temperature.

3. Evaporation zone stability conditions

The profile of the evaporation zone is determined by the casting speed, evaporation rate, and the contact angle of the solution on the substrate (or on the deposited solid layer, especially for low molecular weight materials). The meniscus shape is stable if the volume of the solvent evaporated in a time dt equals the volume of the solution supplied to the nozzle. To a first approximation, assuming a triangular meniscus, we have

$$Sdx = \frac{V_e S}{\rho \sin\theta} dt \tag{1}$$

where V_e is the evaporation rate [kg/(m^2·sec)], ρ is the solvent density, θ is the contact angle which depends on surface tension, the kind of substrate, and the casting speed, and S is the nozzle cross-section; $S = hl$, where h denotes the nozzle height and l the width of the deposition zone.

The casting speed $v_s = dx/dt$ is thus related to the evaporation rate and contact angle:

$$v_s = \frac{V_e}{\rho \sin \Theta} \tag{2}$$

The contact angle cannot change too much (otherwise the solution/substrate contact is broken and the process is no longer stationary but step-wise). Therefore, the casting speed cannot be changed too much unless the evaporation rate is changed, for example by changing the casting temperature.

4. Phase separation conditions

The driving force of the orientation and anisotropy of the layer being formed is the solute concentration gradient in the region where the critical concentration is reached. The concentration profile depends on the relation between the solution supply rate, diffusion coefficient, and evaporation rate. Due to solvent evaporation, the solute concentration is not uniform in the evaporation zone. It increases from the initial concentration in the nozzle, in the casting direction, until the critical concentration for phase separation is reached.

The concentration profile depends on the relation between the evaporation rate and solute diffusion coefficient D. The critical concentration can be reached in different zones of the meniscus, and the direction of the concentration gradient can be different depending on the relationship between these parameters. Figure 2 presents the results of simulations of the solute concentration profile for two different ratios of the casting rate and diffusion coefficient, namely for $k = 10^4$ and 10^5. The simulation parameters were chosen arbitrarily, but were close to the range covered in the experiment (e.g., $D = 10^{-9}$ m^2/sec and a casting speed $v_s = 10^{-5}$ m/sec). The concentration dependence of D is neglected. The black region can be considered to be the region where the critical concentration is reached and phase separation takes place. One can see that for high k the concentration gradient is low and parallel to the casting direction. The critical concentration is reached close to the end of the evaporation zone. Orientation in the obtained layer is parallel to the casting direction. For larger k, the concentration gradient is high, but perpendicular to the solvent surface and not to the casting direction. The critical concentration is reached far from the end of the evaporation zone. Orientation in the layer obtained under such conditions (if the layer has any important anisotropy) is perpendicular to the surface.

A suitable choice of the parameters, in order to obtain a proper concentration gradient, is a necessary but not sufficient condition to obtain a continuous layer, since the casting speed must also match the crystallisation rate (or more generally, the phase separation rate).

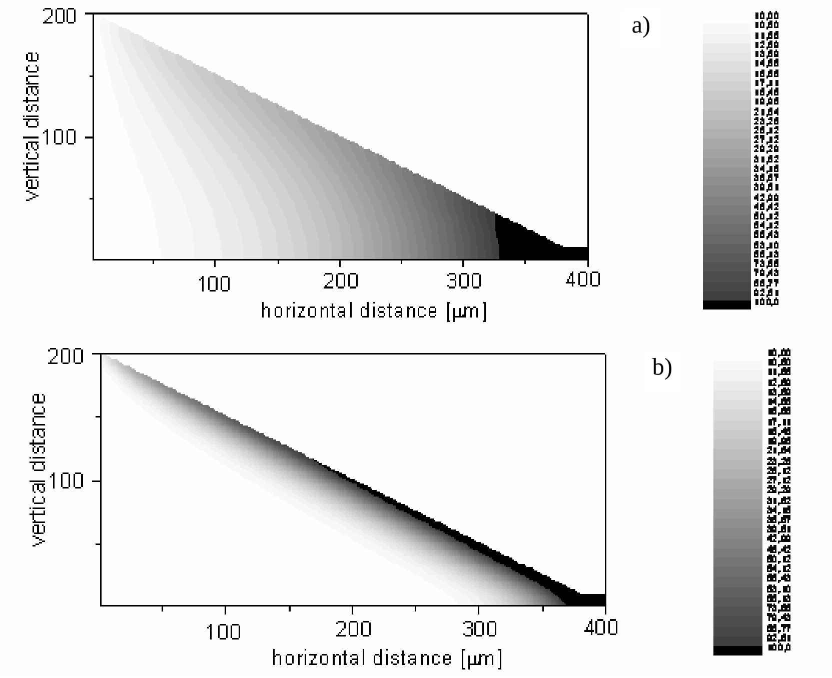

Fig. 2. Simulated solute concentration profile near the end of the evaporation zone for a slow and fast casting rate, relative to the diffusion coefficient $k = 10^4$ (a) and $k = 10^5$ (b)

5. Equipment

Figure 3 shows the zone casting equipment constructed at our laboratory. It consists of two heating blocks mounted on a metal substrate. The upper block houses a syringe used to continuously supply the solution to the nozzle. The substrate, on

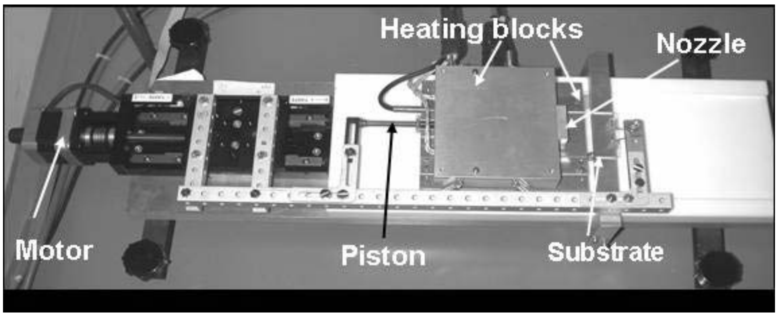

Fig. 3. Zone casting equipment

which the film is cast, is moved on the surface of the lower block. A step motor is used to move the piston in the syringe and the substrate. In other versions, a second motor drives the substrate independently. Temperatures and velocities are controlled electronically.

6. Selected applications

The first reported application of the zone casting technique was a successful preparation of anisotropic polymer/organic metal composites [1–5]. Highly oriented networks, micro- or nanowires of the molecular metal tetrathiotetracene-tetracyanoquinodimethane (TTT-TCNQ), embedded in a polymer matrix, were obtained (Fig. 4).

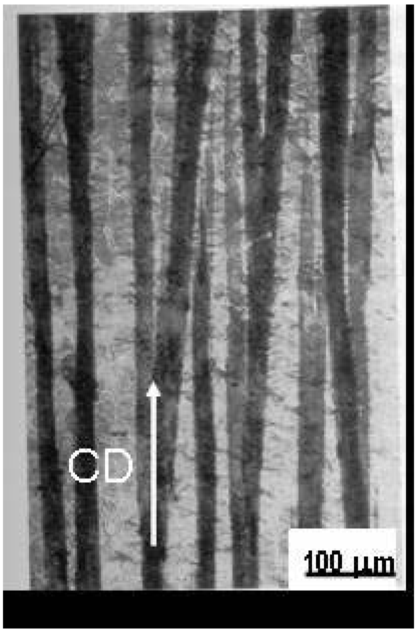

Fig. 4. Highly oriented network of TTT-TCNQ microcrystals in a polypropylene matrix. The arrow shows the casting direction (see [3] for details)

The systems exhibit a very high anisotropy of electrical conductivity (10^6) [1–4]. TTT-TCNQ networks in polypropylene (PP) also show a high anisotropy of optical properties, which allows the excitations that have transitions in the direction perpendicular and parallel to the long axis of the crystal to be identified [5]. Recently, oriented anisotropic thin layers of a discotic compound hexabenzocoronene derivative (HBC-C_{12}) of good quality have been obtained [6, 7]. They have good orientation on an area of square centimetres, with a highly ordered columnar structure and large coherence length, as evidenced by atomic force microscopy images (Fig. 5). Such layers have been shown to act as optical molecular switches [8] and active layers in organic field effect transistors [9, 10]. Other discotic compounds of perylene and HBC derivatives have also been used, and it has been shown that such layers have highly anisotropic optoelectric properties [7, 10]. Preliminary results have also been obtained for other low molecular-weight materials. Highly optically anisotropic thin layers of metallorganic dyes on glass have been obtained, in which the orientation in the obtained layer and the orientation of the optical axes is parallel to the casting direction (in cooperation with A. Pucci, F. Ciardelli, Universiti di Pisa, Dipartimentà di Chimica e Chimica Industriale, Italy).

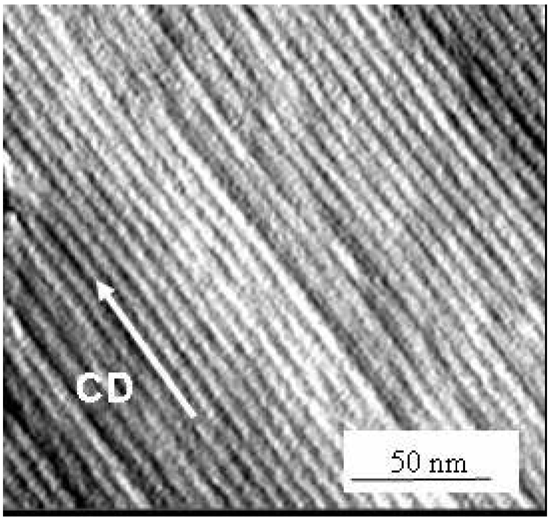

Fig. 5. AFM image of the columnar structure of a zone-cast film of HBC-C_{12}. The arrow shows the casting direction (see [6] for details)

Very recently, we have found that the ZC technique can also be applied to obtain orientation in another class of materials – block copolymers. Phase separation in diblock copolymers leads to the formation of various morphological structures (cylinders, spheres, etc.), depending on block length and external conditions. We were able to obtain thin layers of highly oriented cylinders (in cooperation with T. Kowalewski and K. Matyjaszewski, Carnegie Mellon University, Pittsburgh PA, USA). An interesting feature of this system is that the long axis of the cylinders is oriented perpendicular to the casting direction (Fig. 6).

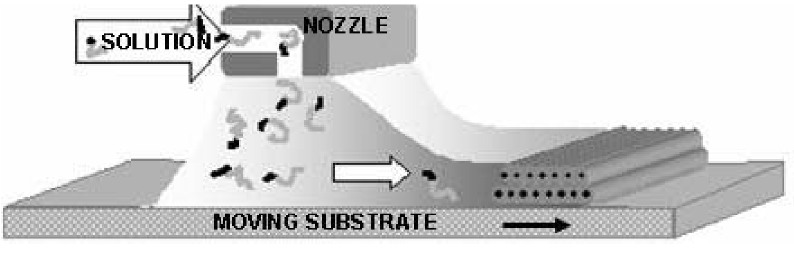

Fig. 6. The formation of the ordered cylinder morphology of a diblock copolymer zone-cast film

7. Conclusions

Zone casting makes possible a continuous deposition of anisotropic layers of soluble materials. For each compound, stationary deposition conditions must be determined by choosing a proper solvent, initial concentration, and adjusting casting parameters such as temperature and casting speed. Under the appropriate conditions, the zone-cast films that are uniform in the centimetre scale and exhibit highly anisotropic macroscopic properties can be obtained for many compounds. The presented examples of different zone-cast materials (low molecular-weight conductors, discotic molecules, oligomers, and copolymers), which can be successfully processed using zone-casting, demonstrate the universality of this technique.

Acknowledgement

The work was supported in part by the State Committee for Scientific (KBN) project T08E 044 23 (2002–2005) and by the Fifth Framework Programme DESMOL (ICA1-CT-2000-70021).

References

[1] TRACZ A., ULAŃSKI J., PAKULA T., KRYSZEWSKI M., Polish Patent P-131986 (1986).

[2] BURDA L., TRACZ A., PAKULA T., ULANSKI J., KRYSZEWSKI M., J. Phys. D: Appl. Phys., 16 (1983), 1737.

[3] TRACZ A., EL SHAFEE E., ULANSKI J., JESZKA J.K., KRYSZEWSKI M., Mater. Sci., 14 (1988), 181.

[4] TRACZ A., EL SHAFEE E., ULANSKI J., JESZKA J.K., KRYSZEWSKI M., [in:] H. Kutzmany, M. Mehring, S. Roth (Eds.), *Electronic Properties of Conjugated Polymers*, Springer-Verlag, Berlin, 1989, p. 442–447.

[5] TRACZ A., EL SHAFEE E., ULANSKI J., JESZKA J.K., KRYSZEWSKI M., Synth. Met., 37 (1990), 175.

[6] TRACZ A., JESZKA J.K., WATSON M.D., PISULA W., MÜLLEN K., PAKULA T., J. Am. Chem. Soc., 125 (2003), 1682.

[7] MISKIEWICZ P., RYBAK A., JUNG J., GLOWACKI I., ULANSKI J., GEERTS Y., WATSON M., MÜLLEN K., Synth. Met., 137 (2003), 905.

[8] PIRIS J., PISULA W., TRACZ A., PAKULA T., MÜLLEN K., WARMAN J.M., Liq. Cryst., 31 (2004), 993.

[9] PISULA W., MENON A., STEPPUTAT M., LIEBERWIRTH I., KOLB U., TRACZ A., PAKULA T., MÜLLEN K., Adv. Mater., accepted)2005).

[10] MIŚKIEWICZ P., RYBAK A., JUNG J., GLOWACKI I., ULAŃSKI J., TRACZ A., PISULA W., PAKULA T., MÜLLEN K., PFLEGER J., Conference on New Concepts and Materials for Molecular Electronics and Nanotechnology, Poznań 2004, Conf. Abstracts, p. 20.

Received 20 October 2004
Revised 3 November 2004