Molecular packing in organic anisotropic media: effects of piesothermal factors on optical transmission in polycrystalline samples

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Received October 27, 2008

Optical transmission was measured for pellets made of polycrystalline powders of stilbene and *p*-terphenyl subject to pressure compaction at temperatures close to the melting point. As compared with similar samples obtained by compaction at room temperature, the transparence was substantially higher, with this difference being more pronounced at higher treatment temperatures and smaller grain size of the initial powder; also, the effect observed was noticeably stronger for *trans*-stilbene than for *p*-terphenyl. The obtained results can be explained in terms of local melting and liquid crystalline ordering of the molecules in outer layers of neighboring grains, resulting in more uniform structuring. Since the measured transparence of the samples showed good correlation with the luminescence light yield for short-range alpha-radiation, this approach can also be used as a method for express analysis of the pellet quality in experimental optimization of preparation conditions of polycrystalline organic scintillators.

Исследовано оптическое пропускание образцов поликристаллических порошков стильбена *п*-терфенила, подверженных прессованию при температурах, близких к точке плавления. По сравнению с аналогичными образцами, запрессованными при комнатной температуре, пропускание значительно увеличивалось, причем это различие возрастало с повышением температуры и уменьшением размеров зерен. Данный эффект был заметно более выражен для *транс*-стильбена по сравнению с *п*-терфенилом. Полученные результаты интерпретируются в терминах локального плавления и жидкокристаллического упорядочения молекул во внешних слоях соседних зерен. Поскольку прозрачность образцов хорошо коррелирует со световыходом люминесценции для короткопробежного альфа-излучения, данный подход можно использовать для экспресс-анализа качества прессованных образцов поликристаллических органических сцинтилляторов.

Organic polycrystalline scintillators obtained by pressure compaction of powder of an appropriate substance (e.g., stilbene, *p*-terphenyl, anthracene, etc.) are new promising materials that could be useful in many application fields [1–3]. In detection of short-range radiation, optical transparence of the scintillation material is expected to be among the major factors affecting the light output — the initial radiation (e.g., alpha-particles) is absorbed in the surface-adjacent layer, while the emerging scintillations are recorded after passing through all the material thickness. In this relationship, the objective of this work was to study the effects of various parameters of the pressure compaction process (temperature, applied pressure, grain size of the powder used) upon optical transparence of the obtained polycrystalline samples.

To prepare polycrystalline samples of stilbene and *p*-terphenyl, melt-grown single crystal ingots of these substances were ground to powder under a liquid nitrogen

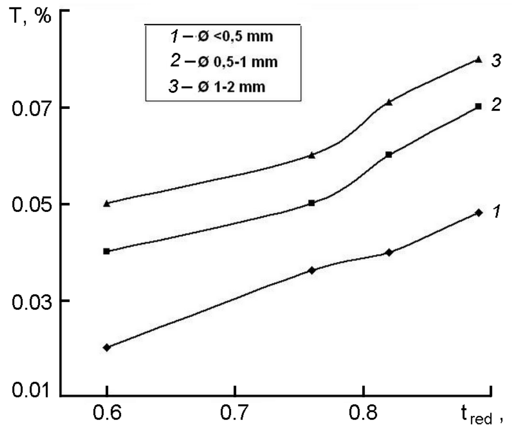

Fig. 1. Optical transmission of the pressure-compacted p-terphenyl samples (without the integrating sphere).

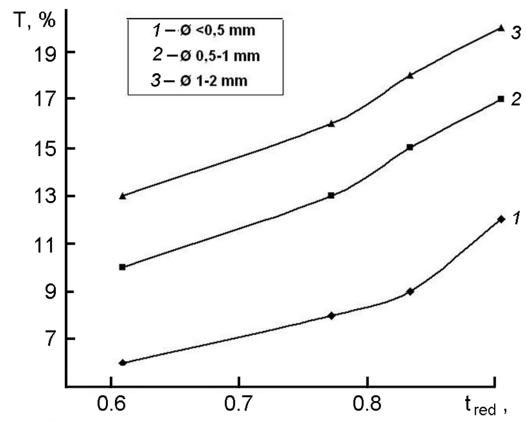

Fig. 2. Optical transmission of the pressure-compacted p-terphenyl samples (with the integrating sphere).

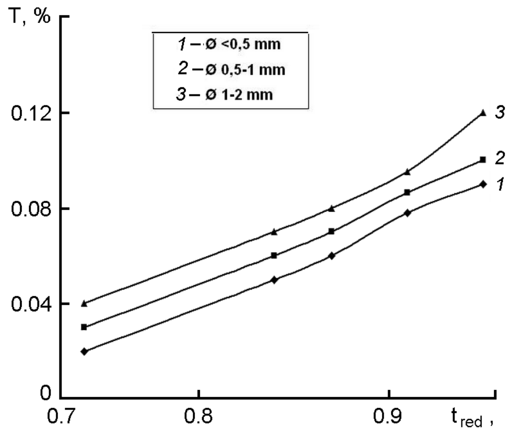

Fig. 3. Optical transmission of the pressure-compacted stilbene samples (without the integrating sphere).

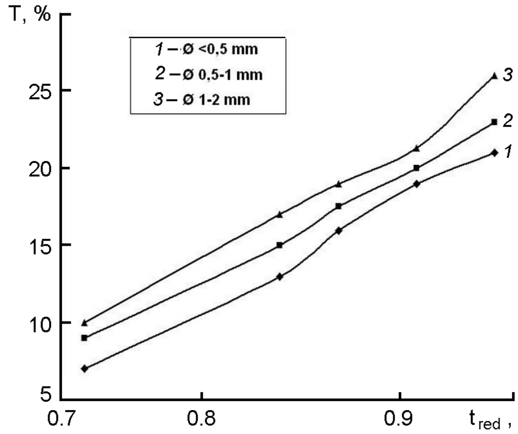

Fig. 4. Optical transmission of the pressure-compacted stilbene samples (with the integrating sphere).

layer. The obtained grains were dried and sorted out into fractions with linear dimensions of grains $d < 0.5$ mm, 0.5...1 mm, and 1...2 mm, using the appropriate sieves. Powders of each fraction were subject to thermal treatment in a rigid mould with simultaneous application of hydrostatic pressure P 300 MPa. The obtained pressure-compacted samples were cylinder-shaped, 30 mm in diameter and 2 mm thick.

Optical transmission of the pressure-compacted stilbene and p-terphenyl samples was measured using a Hitachi 330 spectrophotometer. The measurements were carried out by two different methods — with and without the integrating sphere. The results obtained are shown in Fig. 1–4 as function of the relative compaction temperature $t_{red} = T_{comp}/T_m$, where T_m is the melting point (397 K for stilbene and 487 K for p-terphenyl), t_{red} — reduced temperature. Without the integrating sphere, the measured transmission values are very small — on its way through a polycrystalline sample, only a small fraction of the incident light goes out along the same direction because of scattering on grain boundaries. With the integrating sphere, most of the scattered light is collected back into a beam that reaches the PMT of the spectrophotometer. It is interesting to note that qualitative character of the results is essentially the same in both cases.

The measured transmittance increased by up to 2–3 times when the compaction temperatures rose from the room temperature to the region close to the melting point. (The limiting conditions can be designed, in technology terms, as "cold" and "hot" pressure compaction). Another anticipated result was that larger grain sizes of initial

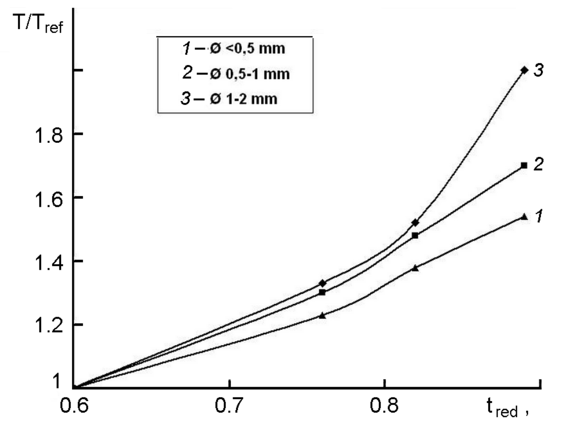

Fig. 5. The relative increase in transmission with temperature for pressure-compacted *p*-terphenyl samples (T_{ref} are transmission values of samples compacted at room temperature).

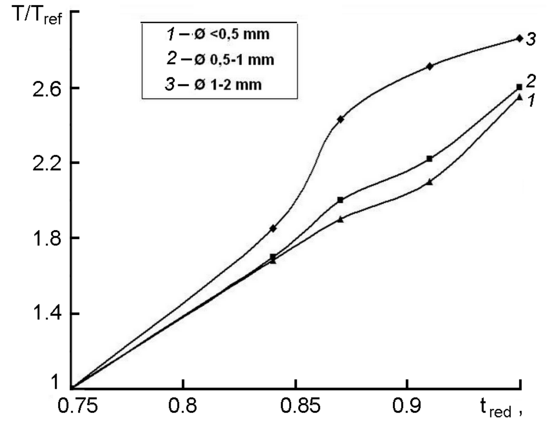

Fig. 6. The relative increase in transmission with temperature for pressure-compacted stilbene samples.

powders led to higher transparence under similar compaction conditions.

To better assess the difference in piesothermic behavior of stilbene and *p*-terphenyl powders, we have calculated the relative increase in transmission with temperature (Fig. 5,6). Here T_{ref} are transmission values of samples compacted at room temperature.

In the case of stilbene, the influence of piesothermic factors results in much stronger response as compared with *p*-terphenyl (maximum obtained increase in transmission by 2.9 times and by 2 times, respectively). This can be explained by differences in steric aspects of the molecular structure. The *p*-terphenyl molecule is essentially rigid, with rotations of aromatic rings around the long molecular axis almost completely suppressed — the aromatic rings are known to be parallel in the solid state [4]. As for stilbene in *trans*-conformation, the molecular packing spontaneously emerging upon crystallization is, in fact, not the densest packing possible, and further application of pressure in combination with premelting temperatures allowing more freedom of molecular movement can probably lead to a more ordered structure.

These results evoke and support our earlier assumption [5] on a possible mechanism involved. Pressure-induced changes in intermolecular distances favour anisotropic intermolecular interactions, which, under conditions of certain molecular mobility at premelting temperatures, can lead to liquid crystal-like orientational ordering of the molecules from the neighbouring domains (grains). The emerging larger single crystalline sections of the compacted sample can possibly be formed via a virtual smectic-B phase, with the relative freedom of molecular movement described by order parameters close but essentially not equal to 1. Further studies on pressure-compacted polycrystals, including mixed systems [6], could give more evidence on this phenomenon.

From the viewpoint of applications, one should note good correlation between optical transparency of the studied samples and their scintillation light output under excitation by alpha-particles (Table). It can be seen that more transparent samples (pressure-compacted at higher temperatures) showed substantially higher light output, especially marked in the case of excitation by for excitation by α-particles. In fact, such treatment improves structural perfection on distances comparable with the free path of α-particle (~30 μm in our case), but cannot affect the perfection of sections with

Table. Relative light output J of polycrystalline samples of stilbene obtained by "cold" and "hot" pressure compaction

Pressure compaction type	Grain size of initial powder, mm	J, %	
		Conversion electrons, 0.622 MeV	α-particles, 5.15 MeV
Cold	from 0.5 to 1	60	21.5
Cold	from 1 to 2	59	25.5
Cold	> 2	97	21
Hot	from 0.5 to 1	102	104
Hot	from 1 to 2	117	126
Hot	> 2	115	122

dimensions comparable with the free path of conversion electrons (~1.8 mm).

In this respect, measurements of optical transparency as described in our paper can be used as a method for rapid quality analysis of pressure-compacted organic scintillators in the process of optimization of the preparation conditions.

References

1. S.V.Budakovsky, N.Z.Galunov, A.Yu.Rybalko et al., *Mol.Cryst.Liq.Cryst.*, **385**, 71 (2002).
2. N.Z.Galunov, J.H.Baker, S.V.Budakovsky et al., *J.Luminescence*, **101–102**, 464 (2003).
3. S.V.Budakovsky, N.Z.Galunov, N.L.Karavaeva et al., *IEEE Trans.Nucl.Sci.*, **54**, 273 (2007).
4. A.I.Kitaigorodskii, Organic Crystallochemistry, ed. AN SSSR, Moscow (1955), p.18 [in Russian].
5. S.V.Budakovski, L.N.Lisetski, P.P.Shtifanyuk, in: Eur. Conf. on Liquid Crystals, Zakopane, Poland (1997), p.122.
6. M.C.Etter, S.M.Reutzel, C.G.Choo, *J.Am.Chem.Soc.*, **115**, 4411 (1993).

Молекулярне пакування в органічних анізотропних середовищах: вплив п'єзотермічних факторів на оптичне пропускання у полікристалічних зразках

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Досліджено оптичне пропускання для зразків полікристалічних порошків стильбену та *n*-терфенілу, які було піддано пресуванню при температурах, близьких до точки плавлення. У порівнянні з аналогічними зразками, пресованими при кімнатній температурі, пропускання значно збільшувалося, причому ця різниця зростала з підвищенням температури пресування і зменшенням розміру зерен. Цей ефект був помітно сильнішим для *транс*-стильбену у порівнянні з *n*-терфенілом. Отримані результати можна пояснити у термінах локального плавлення та рідкокристалічного впорядкування молекул у зовнішніх шарах сусідніх зерен. Оскільки прозорість зразків добре корелювала з світловим виходом люмінесценції для короткопробіжного альфа-випромінювання, цей підхід може бути використаний для експрес-аналізу якості пресованих зразків полікристалічних органічних сцинтиляторів.