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A. V. Vlasov, L. G. Tokareva, D. Ya. Tsvankin,

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Abstract

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**A. V. Vlasov, L. G. Tokareva, D. Ya. Tsvankin,
B. L. Tsetlin, M. V. Shablygin**

Preparation of Oriented Polyvinylidene Chloride by Radiation Polymerization from the Gas Phase on Oriented Polymer Substrates

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It was shown earlier that, under conditions of polymerization of monomers from the gas phase on stretched polymer substrates, the oriented macromolecules of the latter can direct the growth of polymer chains, as a result of which the new polymer is also formed in an oriented state (1). This phenomenon was investigated using as an example the polymerization of acrylonitrile on stretched capron fiber. The orientation of the grafted polyacrylonitrile was determined by the method of IR spectroscopy in polarized light. A pronounced dichroism of IR absorption was found for the band at 2235 cm^{-1}, corresponding to the valence vibrations of the C N group; its sign coincides with the sign of the dichroism of the stretched polyacrylonitrile fiber "nitron." Thermomechanical investigation of combined grafted fibers also confirmed the presence of orientation in a number of polymers obtained by gas-phase polymerization on stretched polyethylene and polyamide fibers (2).

However, attempts to apply the X-ray diffraction method to detect orientation of the polymer in the grafted layer proved unsuccessful. Reflections from grafted polyacrylonitrile and similar polymers were generally absent from the X-ray patterns, apparently owing to the looseness of the structure, the cause of which is the poor crystallizability of these polymers. In accordance with this, the "ordering" of acrylonitrile polymerization decreases as the grafted layer becomes thicker.

It was natural to expect that the effect of "matrix" oriented polymerization would be more distinct if the polymer synthesized under conditions of gas-phase polymerization on oriented substrates crystallizes readily. Then a certain order imposed by the oriented substrate in the process of formation of polymer chains would subsequently, in the course of polymerization, be maintained by highly ordered oriented crystallites of the grafted polymer itself. The present work is devoted to an experimental verification of this assumption.

As the monomer giving a readily crystallizing polymer, vinylidene chloride

Fig. 1

Figure 1: Fig. 1

(VDC) was chosen. The oriented polymer substrate on which radiation gas-phase polymerization of VDC was carried out was a uniaxially stretched polyethylene film obtained from high-pressure polyethylene. The gas-phase polymerization reaction of VDC was carried out in a two-chamber glass apparatus ([3]), which made it possible to irradiate the films in the presence of VDC vapor under conditions excluding the possibility of condensation. Irradiation was carried out using an industrial X-ray unit of the RUP-200 type. The dose rate was 6 rad/sec. The temperature of the film during irradiation was 60°, and the vapor pressure of the monomer was 500 mm Hg. Under these conditions, the graft polymerization

vinylidene chloride proceeds at a rate of 5 percent per hour relative to the initial weight of the film (radiation yield: 1500 monomer molecules per 100 eV).

Fig. 1 presents the IR absorption spectrum of a combined film obtained by radiation gas-phase polymerization of vinylidene chloride on a stretched polyethylene film. In the same figure, for comparison, IR absorption spectra are given for two combined films obtained by polymerization of VDC under the same conditions on unstretched polyethylene films, one of which was then subjected to subsequent mechanical stretching. The IR spectra were recorded on a Hilger H-800 instrument with a sodium chloride prism and a selenium polarizer.

Fig. 1. Regions of the IR polarization spectra of combined films obtained by radiation polymerization of vinylidene chloride from the gas phase on polyethylene films.
a –polymerization on a stretched film; *b* –polymerization on an unstretched film followed by mechanical stretching; *c* –polymerization on an unstretched film.

Examination of the spectra presented confirms the supposition made. Indeed, grafted PVDC obtained by polymerization on a stretched polyethylene film exhibits substantial perpendicular dichroism (value 0.35–0.40) for the absorption bands at 1046 and 1070 cm^{-1}, corresponding to stretching vibrations of the CCl_2 group (Fig. 1*a*). During polymerization on an unstretched film, an unoriented polymer is formed (Fig. 1*b*). As a result of stretching such a film, the grafted unoriented PVDC is oriented in the same way as the polyethylene substrate (Fig. 1*c*). It should be noted, however, that the spectra of oriented PVDC obtained directly by polymerization on a stretched polyethylene film and of grafted PVDC oriented by stretching after grafting onto an unstretched polyethylene film are not identical, as is seen from a comparison of Fig. 1*a* and Fig. 1*c*: the characteristic absorption bands mentioned above have different relative dichroism; in the spectrum of Fig. 1*a*, new absorption bands are observed at 1025 cm^{-1} with parallel dichroism and at 1010 cm^{-1}, which are absent in the spectrum of Fig. 1*c*, corresponding to the film stretched after grafting, and

Fig. 2. X-ray diffraction pattern of a composite film containing 55% polyvinylidene chloride

Figure 2: Fig. 2. X-ray diffraction pattern of a composite film containing 55% polyvinylidene chloride

Fig. 3. Molecular model of a grafted polyvinylidene chloride chain arranged along a polyethylene chain

Figure 3: Fig. 3. Molecular model of a grafted polyvinylidene chloride chain arranged along a polyethylene chain

which have not been described in the literature (4). This permits the conclusion that PVDC obtained by radiation gas-phase polymerization on oriented polymer substrates has structural features; further investigations are necessary to elucidate their nature.

Fig. 2 gives the X-ray diffraction pattern of a combined film obtained by gas-phase polymerization of VDC on a stretched polyethylene film with a content of 55% grafted polymer. In the X-ray diffraction pattern, reflections corresponding to the structure of PVDC (5) are clearly manifested. On the non-zero layer lines of the X-ray diffraction pattern, the 020 and 212 reflections of PVDC are marked. On the zero layer line, three reflections are marked. The one closest to the center of the X-ray diffraction pattern is the 400, $20\bar{2}$, and 202 reflection of PVDC. The middle reflection is $40\bar{2}$ and 402 of PVDC and 110 of polyethylene. The reflection farthest from the center is ···

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Fig. 2. X-ray diffraction pattern of a composite film containing 55% polyvinylidene chloride

lex is the 200 reflection of polyethylene. X-ray diffraction patterns of films with different contents of grafted polymer show that PVDC reflections appear already when its content in the film is 5–7%. The X-ray diffraction patterns show a sufficiently high degree of crystallinity of the grafted PVDC and—in accordance with the assumption made and in agreement with IR-spectroscopy data—a high degree of orientation. The order imposed by the substrate in the formation of polymer chains is preserved even in very thick layers of grafted PVDC. It should be especially noted that obtaining PVDC in an oriented state by other methods is in general difficult, since the polymer decomposes before melting and has no good solvents.

Fig. 3. Molecular model of a grafted polyvinylidene chloride chain arranged along a polyethylene chain

Thus, the X-ray investigation of the combined films obtained in the present work provides a third independent experimental proof of the validity of the assumption made, namely that under conditions of gas-phase polymerization on drawn polymer substrates, direct synthesis of oriented structures is accomplished. This effect, which has a certain similarity to the phenomenon of epitaxy in the formation of organic crystals from the gas phase on various solid substrates [6], differs fundamentally from the latter in that crystal growth occurs simultaneously with the chemical reaction of formation of polymer chains, and precisely as a result of this, directed "epitaxial" polymerization can be realized. The latter takes place because the oriented polymer substrate tends to create an analogous orientation in the polymer chains growing on it. Of course, of decisive importance here, as was indicated earlier (1, 2), is the absence, under the conditions of the gas-phase process, of a second condensed phase, whose presence would sharply reduce the gain in the interaction energy of the growing polymer chains with the substrate and would lead to disordered polymerization because of the entropic factor.

Figure 3 presents a molecular model showing the possibility of growth of a PVDC polymer chain along a drawn polyethylene macromolecule. The initiation of the VDC polymerization reaction here is the act of addition of a monomer molecule to a polymer radical obtained as a result of abstraction of a hydrogen atom from the polyethylene macromolecule (the "grafting" site is indicated in the figure by an arrow).

It is evident that the oriented polymer formations obtained in the present work by a nonmechanical route as a result of direct synthesis and possessing a sufficiently high degree of crystallinity and orientation must differ in their structure and properties from ordinary oriented polymers. Elucidation of the new possibilities opened up by this method of obtaining oriented structures is the subject of our further investigations.

It should be noted that the radiation method of initiating gas-phase polymerization on oriented substrates was chosen as the simplest and most universal one; in principle, however, other methods of initiating chain processes may also be used. It also seems to us that a synthesis of oriented structures on substrates similar to that described can be carried out not only by polymerization, but also by polycondensation.

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Institute of Organoelement Compounds
Academy of Sciences of the USSR

All-Union Scientific Research Institute
of Artificial Fiber

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Note: Figure translations are in progress. See original paper for figures.