PLASMA AND VACUUM ULTRAVIOLET INITIATED POLYMERIZATION OF MESOGENIC MONOMERS ON THE SURFACE OF FLUOROCARBON POLYMERS.

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Abstract.

Graft post polymerization of mesogenic monomer onto fluorine-containing polymer support was initiated by the action of gas discharge plasma and vacuum ultraviolet radiation. The resultant sandwiched structure possesses the combined physical-mechanical properties of the polymer supporting film and optical characteristics of the anisotropic liquid crystalline (LC) polymer layer.

Introduction.

Side chain LC polymers are characterized by the set of specific optical and electrooptical properties. To use these properties for technical applications it is necessary to prepare polymer film having appropriate physical-mechanical characteristics while conventional side chain polymers do not provide it. To combine the main advantages of LC media and polymer materials one can apply the graft polymerization approach.

Several techniques including g-irradiation [1] and low temperature plasma [2] initiation were described to induce grafting of allyl or vinyl monomers onto polymer supports. The most strong modifying effect could be achieved if mesogenic monomers are polymerized on a pretreated surface. This should result in formation of the grafted anisotropic layer which should be sensitive to the temperature and external field.

We have studied the graft post polymerization of 4-cyano-4'-(biphenylyloxy)butyl acrylate which is known to form a nematic homopolymer [3] on to the surface of polytetrafluoroethylene (PTFE) and tetrafluoroethylene-hexafluoropropylene (85:15) copolymer (FEP) activated by gas discharge plasma in vapor of water and vacuum ultraviolet irradiation in the presence of air. The choice of

polymer support is dictated by two reasons: the first one is unique physical-mechanical properties of this type of films and the second- the known ability of fluorine containing peroxides to form stable and active radicals [4] which are necessary to initiate grafting.

Experimental.

The monomer was synthesized as described in [3]. PTFE and FEP films used are semicrystalline materials with melting points 327 and 270 ^{o}C correspondingly.

A flow-type cylindrical reactor was used for plasma treatment of polymer substrates. Air, O_2, Ar, CO_2, H_2O were introduced into reactor tube where the discharge was maintained by means of two external electrodes. A generator of frequency 13.56MHz was used to produce the discharge. The temperature of substrate was controlled and maintained in the region 10-200 ^{o}C. A process of plasma treatment was performed at discharge power 10-100 W, gas pressure 0,01-10 Torr, flow rate 1-1000 cm^3(STP)/min in the case of discharge in air and at gas pressure 0,01-10 Torr, flow rate 1-10 cm^3(STP)/min in the case of discharge in water vapor. It was studied maximum concentration of radical products took place in the case of discharge in water vapor.

VUV irradiation was carried out in vacuum chamber at air pressure 0,1-100Torr, flow rate 20-60 sm^3(STP)/min and room temperature. The hollow discharge gas resonant Xe lamp KsR-2A [5] equipped with MgF_2 window and located at a distance 30 mm from polymer surface has been used. The radiation intensity was measured by "sun blind" photodiod. After plasma and VUV treatment polymer substrate was held in the contact with mesogenic monomer at different temperatures in vacuum chamber at the pressure 10^{-2} Torr.

IR spectra were recorded with Perkin-Elmer 1720X FTIR spectrometer using transmission and attenuated total reflection (ATR) technique (Harick ATR attachment, KRS-5 prism, 45^{o} angle, 25 reflections). ESR spectra were recorded with AE 4700 ESR spectrometer (Minsk).

Metler DSC (TA 4000) was used to investigate the thermal behavior of initial and grafted samples. Optical polarizing microscope POLAM L-312 equipped with the heating stage RNMK-05 (Boetius) was used for optical texture observations.

Results and discussion.

ESR spectra of FEP films activated by gas discharge plasma (Fig.1a, curve 1) and by VUV irradiation (Fig.1b, curve 1) indicate the presence of radical products on the irradiated surfaces of polymer films: the spectra are characterized by anasymmetrical singlet with the splitting 20-30 G and g-factor equal to 2.004.

The analysis of the spectra line shapes and their characteristics brings to the conclusion that it is identical to that we have observed before [4] and assigned to chain scission of peroxy radical of $CF_2OO\bullet$ type. Subsequent cleaning of irradiated films in benzene displays the essential distinctions in these methods of polymer films activating.

To demonstrate this difference we compared ESR spectra of polymer films activated by gas discharge plasma and by VUV irradiation after their treatment with benzene (see Fig.1, curves 2). The calculations show that the number of radical products on polymer surface activated by VUV radiation decrease about ten times after treatment in benzene. In the case of gas discharge plasma activating slight fall of radical products concentration (not more that 10%) takes place. These data allow to suppose that under VUV activating of polymer films low molecular weight products play the most important role. At the same time in the case of gas discharge plasma treatment the amount of these products are much less probably due to the process of ion etching.

ATR FTIR spectra of FEP film before (1) and after (2) VUV treatment are given in Fig. 2. It shows that VUV treatment results in the oxidation of a polymer films surface: two new bands at 1884 and 1780 cm^{-1} appear in the spectrum of the treated sample can be Fig. 2 attributed to ν (C=O) vibrations in carboxyl perfluorinated compounds.

This shows that the treatment mentioned above results in the formation of different radical and nonradical oxygen containing species on the FEP polymer film surface. Just the same products are observed after photooxydation of PTFE.

After the monomer layer was set in contact with the radical containing surface one could observe the post polymerization process carrying out in vacuum chamber when the monomer is in the crystalline state ($80^{o}C$) and above the melting point in the isotropic state ($100^{o}C$). After the treatment of the post polymerized sample with benzene and 1,2-dichlorethane/acetonitrile mixture (4:1) to remove the residual monomer and non-grafted homopolymer the main spectral features of the CN-containing grafted polymer are very well seen from the ATR IR spectra (Fig. 3).

New bands at 2922, 2853, 2224, 1729, 1603, 1494, 1397, 1040 and 822 cm^{-1} appear which coincide with those existing in the spectrum of the pure CN-containing acrylic homopolymer [3]. The weight measurements show that grafted polymer fraction is equal to 20-24% of the total amount of the polymer produced in the post polymerization process and it does not depend on the polymerization time. By means of the polarizing microscopy and DSC measurements the structure of the grafted polymer is found to be very similar to that described for the nematic homopolymer [3] with the clearing point equal to $124^{o}C$. This clearing point is the characteristic one for the polymer of the high molecular mass when MM does not influence nematic-isotropic phase transition temperature [3]. It was even possible to indicate the glass transition temperature for the grafted polymer ($55^{o}C$) which is in a good correlation with that measured for a homopolymer. Transitions observed for the grafted side chain polymer proceed within the temperature range corresponding to the crystalline state of the supporting polymer without any visible change in the aggregative state of the film as a whole although optical properties of the sandwiched film strongly change.

It is necessary to draw attention to the fact that contrary to post polymerization processes already known and described in [1,2] where the grafting is realized from the

vapor or liquid monomer state we observe polymerization not only in liquid but also in crystalline phase of monomer which results in LC polymer formation.

In Fig. 4 the thickness of the grafted polymer is given as a function of post polymerization time. The initial rate of graft polymerization dramatically increases (more than ten times) if the monomer changes its phase state from the crystalline (80^{o}C) to an isotropic one (100^{o}C). The possible mechanism of the VUV induced graft post polymerization can be considered as follows: surface active centers react with monomer double bonds and initiate the process of radical polymerization. From this viewpoint it is not clear what is the reason for the formation of high amounts (75%) of the homopolymer which is not bound with the supporting film. One has to take into account at least two reasons. The first one is the formation of two main groups of active centers on the irradiated polymer film: the first group of centers is strongly bound with the supporting film and the second one consists of low molecular weight products of photooxydation process which are really not linked with the surface. The second reason could result from the growing chain transfer to a monomer in the bulk.

Conclusions.

Mesogene-containing monomer was grafted onto polymer support due to VUV induced post polymerization. It results in the formation of the sandwich structure comprised of two layers - fluorine containing polymer which provides physical-mechanical properties which are necessary for polymer film materials and side chain polymer layer which exhibits the main features of a nematic liquid crystal. The opaque birefrigent texture of such sandwiched film can reversibly appear and disappear at the nematic-isotropic phase transition without any change of the aggregative state and shape of the sample as a whole. The transparency of the sandwich film can be also easily controlled by the change of the temperature.

Acknowledgments

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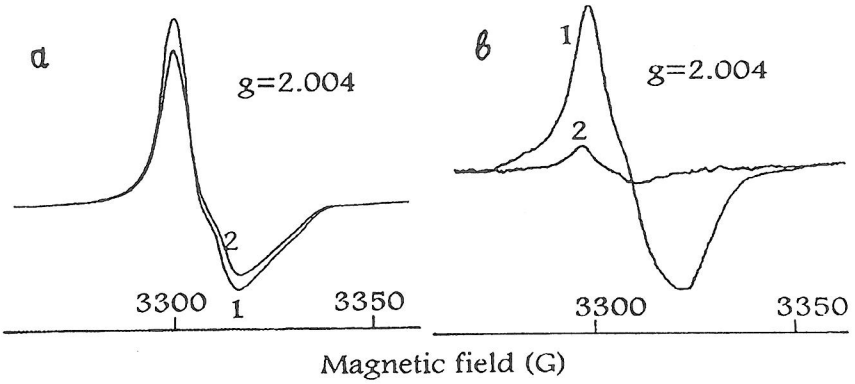

Fig. 1. ESR spectra of FEP films exposed to gas discharge plasma (a) and VUV radiation (b). 1 - just after treatment, 2 - after subsequent cleaning in benzene.

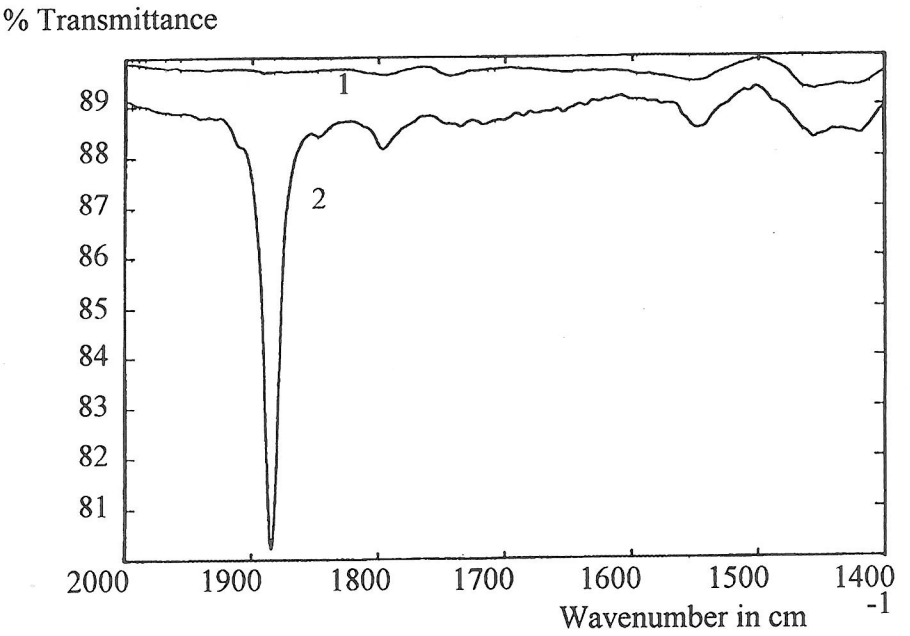

Fig. 2. FTIR ATR spectra of FEP film virgin sample(1) and VUV treated sample(2),

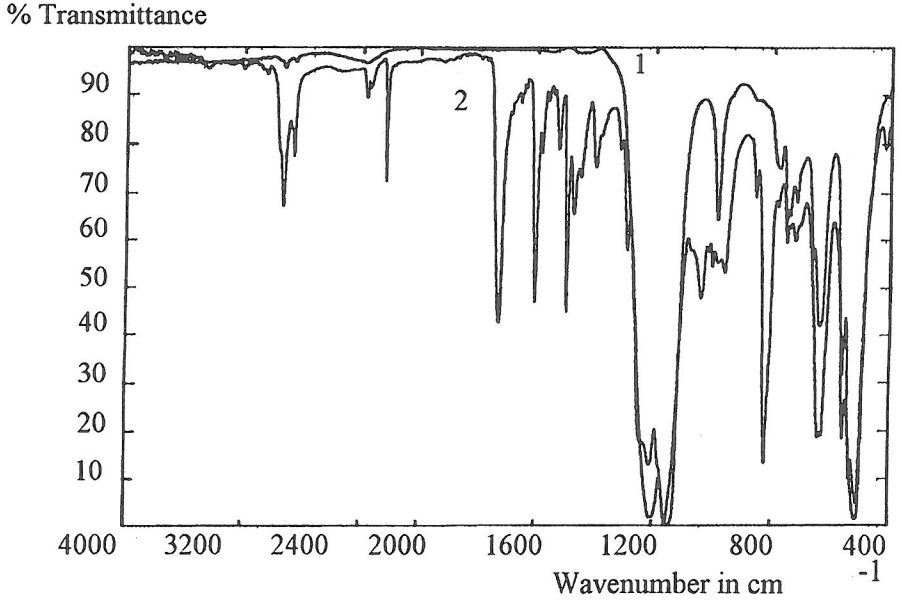

Fig. 3. FTIR ATR spectra of FEP film virgin sample(1) and sandwiched film after graft post polymerization(2).

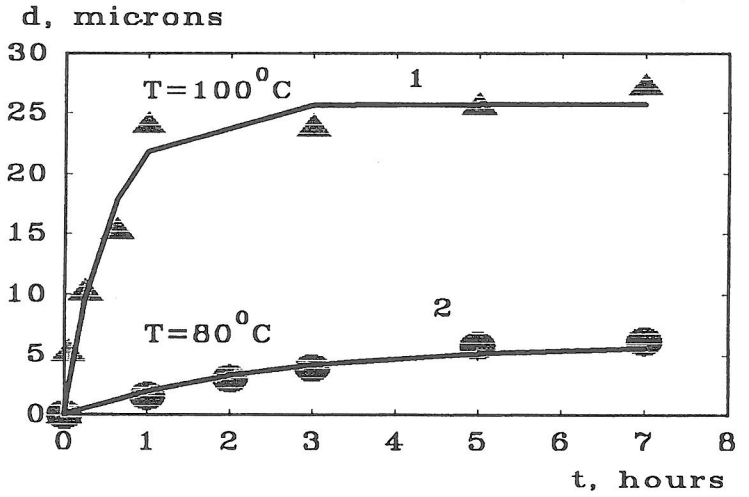

Fig. 4. The thickness of grafted LC polymer film vs. time of post polymerization carried out at different temperatures: 100°C(1), 80°C(2).