

## GRAFT COPOLYMERIZATION OF ACRYLATE MONOMERS ONTO POLYPROPYLENE USING LOW PRESSURE PLASMA<sup>1)</sup>

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The grafting of acrylate monomers onto the polypropylene surface has been obtained by low pressure application of monomer vapours immediately after the rf Ar plasma exposure of the polypropylene. The presence of the graft copolymer was proved by IR spectra (ATR technique), electron microphotography and contact angle measurement. It has been found that even a very small amount of oxygen can stop grafting. The discharge in monomer vapours produces mainly the acrylate homopolymer and causes just a slight increase of the copolymer content.

### ГРАФТ-СОПОЛИМЕРИЗАЦИЯ АКРИЛАТОВЫХ МОНОМЕРОВ НА ПОЛИПРОПИЛЕНЕ ПРИ ПОМОЩИ ПЛАЗМЫ НИЗКОГО ДАВЛЕНИЯ

Прививка акрилатовых мономеров на поверхность полипропилена проводилась при низком давлении паров мономера сразу после воздействия высокочастотной аргоновой плазмы на полипропилен. Наличие графт-сополимера доказано на основе инфракрасных спектров, электронных микрофотографий и измерения контактного угла смачивания. Обнаружено, что даже небольшое количество кислорода может приостановить прививку. Под действием разряда в парах мономера образуется главным образом акрилатовый гомополимер, и этим обусловлено только небольшое количество сополимера.

### 1. INTRODUCTION

During the past few years there has been a steadily growing interest in the use of plasmas for the modification of the surface properties of various solid materials [1,

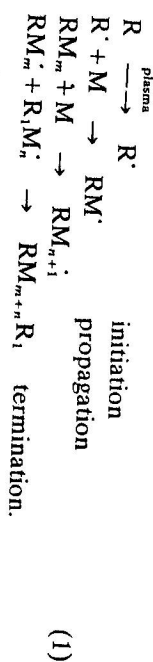
<sup>1)</sup> Contribution presented at the 5th Symposium on Elementary Processes and Chemical Reactions in Low Temperature Plasma, ŠTIAVNICKÉ BANE, May 21—25, 1984.

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2], particularly inert ones like polypropylene (PP) is [3, 4]. This interest has been motivated by the ability of plasmas to produce a big variety of changes on solid surfaces such as the desorption of gases, degradation, removing of layers, crosslinking, chemical reactions, etc. In the case of polymers these changes improve the wettability, the adhesion, the increase of roughness and polar groups [5–8].

With respect to some requirements for improving PP surface properties we studied this polymer in spite of some problems of plasma treatment application to PP. After the washing of the treated foils by common solvents (ethylalcohol, water), there occurs a drastic decrease of active centres (hydroperoxide and carbonyl groups) on the surface of the foil treated before [9]. This effect is explained by the appearance of a new undisturbed PP surface after the degradation layer has been removed from the foil by washing. The layer has no firm (chemical) bonds with the PP subsurface. It seems to be unavoidable to apply some chemical arrangement simultaneously with or just after the plasma treatment to achieve readable chemical changes on the PP surface.

Graft copolymerization offers a complete and radical chemical transformation of the surface [2–4, 10]. Chemically active species and UV radiation present in a plasma affect the polymer surface creating ions, radicals and electronically excited states in a thin surface layer. Provided that graft copolymerization in a plasma is caused by a radical mechanism [10], it can be illustrated by three steps:



When oxygen is present, the free radicals of the polymer usually change into peroxide functional groups that can in principle initiate grafting, for example by the reaction

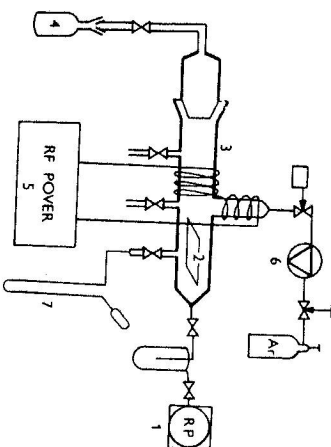


## II. Methods

To obtain a good oxygen desorption from the polypropylene surface and from the reaction chamber walls, and to remove gases from the monomer in order to perform grafting, we employed a low pressure high frequency argon plasma, generated by an inductively coupled rf generator (~1 MHz). The scheme of the experimental equipment is in Fig. 1. For the flow of the working gas Ar we chose the value 0.5 Pa m<sup>3</sup>/s, corresponding to the pressure of 200 Pa inside the vacuum chamber. The rf power absorbed in the discharge (approximately 30 W) was not changed during the experiments. The polymer samples were exposed to the Ar plasma from 5 to 20 seconds.

We studied commercial polypropylene (Trespaphan, Hoechst A G, Kalle) with a biaxial orientation; two monomers were used for grafting — methylmethacrylate (MMA) and ethylacrylate (EA). Gases from inside the monomer were removed before every experiment. We alternated the pumping of the space above the frozen monomer with heating the monomer in a closed space. During exposure of PP in the Ar plasma, the space of the monomer was closed. The place of the monomer was chosen far enough from the plasma region and from the rf power too, to

Fig. 1. Scheme of the experimental equipment for graft copolymerization onto polymer films. 1 — rotary oil pump, 2 — sample, 3 — vacuum chamber, 4 — monomer, 5 — rf generator, 6 — flowmeter, 7 — silicon oil U manometer.



prevent the production of a homopolymer in the closed space of the monomer. Immediately after the exposure we stopped the Ar flow, closed the chamber on the side near the pump and opened the monomer space for 15 minutes to perform the grafting. Before and mainly after the grafting experiment the PP film had been washed carefully for 2 hours in acetone, using a Soxhlet extractor, to extract the rest of the monomer and the unwanted homopolymer. It is supposed that the whole homopolymer content, if there is any, is dissolved and remains in the solution.

To prove the presence of the copolymer on the PP surface we used the IR spectrophotometer Perkin-Elmer 557 with a multireflection arrangement ATR (60° KRS crystal). The contact angles of H<sub>2</sub>O, ethyleneglycol and Br-naphthalene drops were measured twice in 5 places by the Kernco apparatus (USA) and were determined statistically. By means of the scanning electron microscopy SEM JEOL J. S. 35 we obtained the picture of morphological changes of the PP surface. UV spectra were taken by a UV-VIS spectrophotometer, Carl Zeiss, Jena.

## III. RESULTS AND DISCUSSION

We have found that the ATR IR technique is sensitive enough to determine even a low yield of a graft copolymer. Particularly, in the case of polyacrylates there is a strong single absorption band of carbonyl groups (C=O) in the region of the

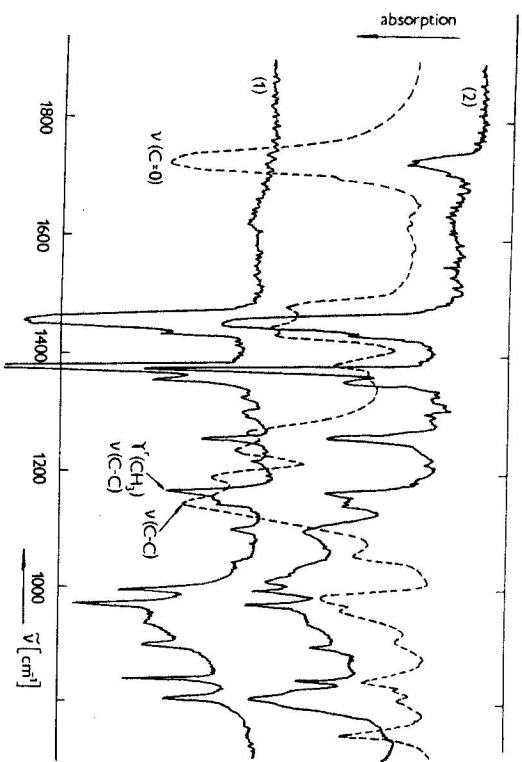
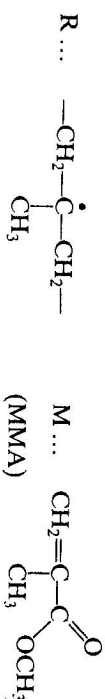


Fig. 2. ATR IR absorption spectra of non grafted (1) and grafted (2) surface of PP by MMA. Dashed line illustrates the pure homopolymer (PMMA) surface.

wave number of about  $1730\text{ cm}^{-1}$  for PMMA, PE, etc. Round this position in the IR spectrum PP has no absorption. This is the reason why we can notice even a very small amount of a polyacrylate grafted onto the PP in the absorption IR spectrum. We can watch the situation in Fig. 2, where an interesting part of the IR spectrum has been chosen. The spectrum of the non-grafted surface belongs to the foil not treated by the Ar plasma, but was immersed into a vacuum chamber with monomer vapours for as long as the plasma treated foils. The same spectrum has the PP surface treated by the Ar plasma without any contact with the monomer. The foils were washed by a solvent (acetone) in a standard way. Therefore the monomer and homopolymer must be completely dissolved in the solution and the peak at  $1730\text{ cm}^{-1}$  really determines the presence of the copolymer. The probable scheme of this copolymer production in the absence of  $\text{O}_2$  is the scheme (1), where R is the most stable PP radical and M the acrylate monomer



In Fig. 3 and Fig. 4 we can follow the dependence of the grafting yield on the Ar plasma exposition time. With regard to our experimental conditions, just a limited number of foils was measured. However, we found a local maximum of 10 seconds

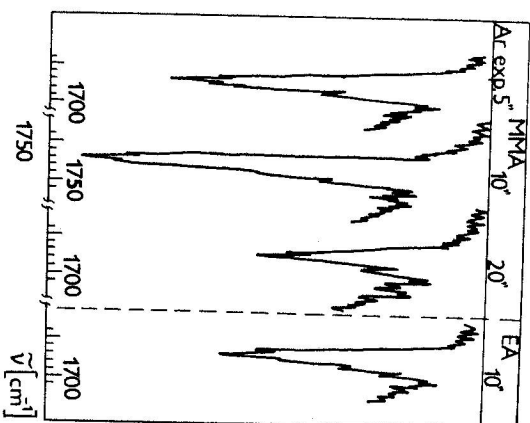


Fig. 3. The dependence of the absorption vibrational band of the carbonyl group ( $\text{C}=\text{O}$ ),  $1730\text{ cm}^{-1}$  on the Ar plasma exposition time.

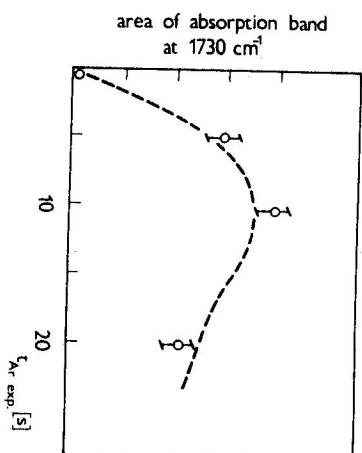


Fig. 4. The Ar plasma exposition time dependence of an amount of the carbonyl groups characterized by the area of a  $1730\text{ cm}^{-1}$  ( $\text{C}=\text{O}$ ) vibrational band of IR absorption spectra.

of the plasma treatment. Graft copolymerization with EA proceeds in a way very similar to that of MMA. When we switched on the discharge also in monomer vapours for a short time (5 sec), the amount of the homopolymer increased but the copolymer yield remained nearly on the same level with little growth. UV spectra also confirm some changes in the PP foils as can be seen in Fig. 5. Microphotographs in Fig. 6 show some morphological changes on the PP surface. The graft copolymer creates small islands on the surface and makes it highly heterogeneous. A summary of the contact angle measurement is in Table 1. The decrease of the contact angle of the grafted PP from the PP value to the PMMA one also confirms the presence of a copolymer. The three liquids chosen have different ratios of polar and disperse surface forces.

Some authors [11] have found new bands at  $887$  and  $910\text{ cm}^{-1}$  in the IR spectra of the He-plasma treated PO. Those can belong to the vinyl and vinylidene groups created in plasma according to the scheme



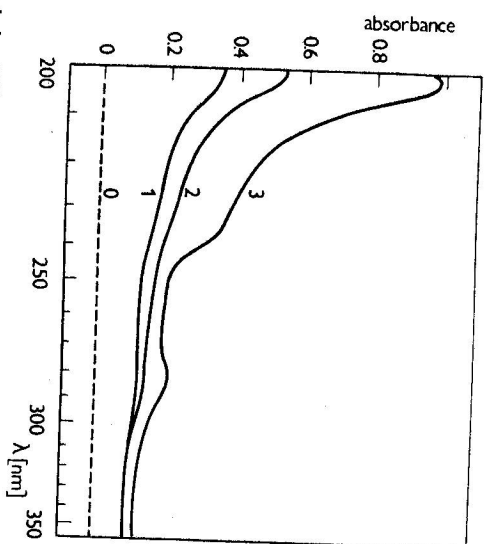


Fig. 5. The transmission UV spectra of the treated PP films. 0 — basic line, 1 — extracted in acetone as every foil, 2 — Ar plasma treatment only, 3 — Ar plasma + grafting in MMA vapours.

In our spectra (Fig. 2) we could read just very small changes at 887, 910  $\text{cm}^{-1}$ . In the spectra of the  $\text{N}_2$  plasma treated PP [12] there did not occur any changes at the mentioned position either.

It is very interesting that we could achieve no grafting on PP using a silent discharge at atmospheric pressure in the air, or in the technical  $\text{N}_2$ . Even a very small addition of the air into a low pressure Ar discharge caused the grafting to vanish. It was confirmed by ESR spectra that in the presence of  $\text{O}_2$  a high long lifetime (many hours) until their transformation to hydroperoxides or to ketones occurs, as shown in the scheme [14, 15]

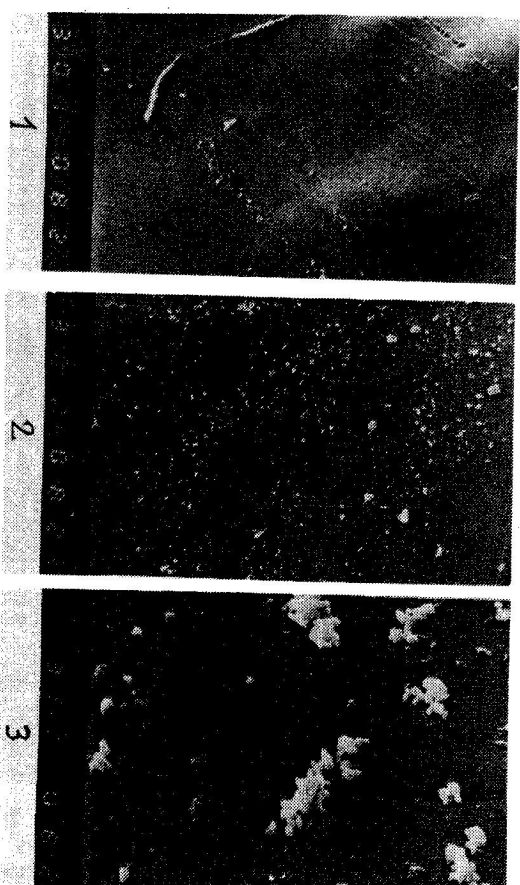
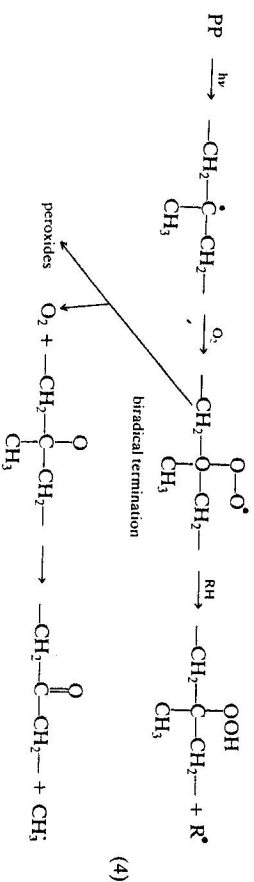


Fig. 6. Photographs of polypropylene surface obtained by SEM. 1 — untreated PP surface, 2 — MMA grafted surface 10 $\times$  Ar, 3 — the same as 2 but 10 times greater (magnification 3000).

It is very likely that peroxoradicals and the hydroperoxides are not able to cause graft copolymerization on PP (according to scheme (2)) without the help of heating or some other auxiliary process. It is possible that even an adsorbed layer of  $\text{O}_2$  on a PP surface can stop grafting. The peroxoradicals and other polymer radicals are probably transformed in the presence of  $\text{O}_2$  to ketones (through the biradical termination according to scheme (4)), which do not cause grafting.

Table 1

liquid drops used for contact angle measurement on PP	contact angle [°]			
	non-grafted PP surface		grafted PP surface	
	10 $\times$ Ar		20 $\times$ Ar	
water	95	70	85	66
ethylene glycol	63	50	60	40
Br-naphthalene	21	15	17	12

temperature during angle measurement 25  $^\circ\text{C}$   
the mean deviation of angle values 2.2 $^\circ$

## REFERENCES

- [1] Hollahan, J. R., Bell, A. T.: *Techniques and Application of Plasma Chemistry*. Wiley-Interscience, New York 1974.
- [2] Shen, M.: *Plasma Chemistry of Polymers*. Marcel Dekker, New York 1976.
- [3] Osada, Y., Iiyaha, Y., Ohta, H.: *Nippon Kagaku Kaishi* 831 (1983).
- [4] Yasuda, H., Sherry, B., El-Nokaly, H. A., Friberg, S. E.: *Appl. Polym. Sci.* 27 (1982), 1735.
- [5] Hall, J. R., Westerdahl, C. A. L., Bondar, M. J., Levi, D. W.: *J. Appl. Polym. Sci.* 16 (1973), 1465.
- [6] Geymer, D. O.: *Macromol. Chem.* 100 (1967), 186.
- [7] Blecha, J., Mastihuba, M., Lapčík, L., Lodes, A., Krupa, P.: *Acta Phys. Slov.* 32 (1982), 333.
- [8] Derco, J., Lodes, A., Lapčík, L., Blecha, J.: *Chem. zvesti (in print)* 1984.
- [9] Topol'sky, I.: *The Study of Hydrophilization of Polypropylene*. Thesis. Bratislava 1983.
- [10] Battaerd, H. A. J., Tregear, G. W.: *Graft Copolymers*. John Wiley and Sons, New York 1967.
- [11] Slovachotova, N. A., Iljichevova, Z. F., Visiljev, A. L., Kargin, V. A.: *Vysokomol. Soedin.* 6 (1964), 608.
- [12] Weininger, J. L.: *J. Phys. Chem.* 65 (1961), 941.
- [13] Pospíšil, L., Janča, J., Ambrož, L.: *Folia Fac. Sci. Nat. Univ. Purkynianae Brunensis*, 18, *Physica* 25, Opus 3 (1977), 67.
- [14] Ranbi, B., Rabek, J. F.: *Forodegradacia, fotooxidacia a fotostabilizacia polimerov*. Mir, Moskva 1978.
- [15] Penot, G., Arnaud, R., Lemaire, J.: *Makromol. Chem.* 183 (1982), 2731.

Received June 8th, 1984

Revised version received July 30th, 1984