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Abstract

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CHEMISTRY

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ON THE PREPARATION OF GRAFT COPOLYMERS OF POLYAMIDES WITH VINYL MONOMERS

Graft copolymers have recently begun to attract increasing attention from researchers, owing to the new synthetic possibilities that they open up. Immergut and Mark (^1) published a review of work on the preparation of graft and block copolymers by various methods. All the methods proposed for this purpose are suitable, however, only for grafting onto polymers in the dissolved state; an exception is the method developed by Shapiro (^2), based on the preliminary action on the polymer of penetrating radiations, leading to cleavage of the molecules and the formation of free macroradicals. In all these methods, in most cases, the simultaneous formation of graft and block copolymers takes place.

We attempted to develop a method for obtaining graft copolymers that would not lead to the simultaneous formation of block copolymers. For this purpose the starting polyamides were subjected to the action of ozone and were then treated with vinyl monomers—styrene or methyl methacrylate. As a result, a layer of graft copolymer was formed on the surface of the polyamide.

First we examined the effect of ozone on polyamides. For this purpose, a capron film was subjected to the action of ozone for various times, from 2 min. to 6 hr., and then its properties were measured.

The results obtained are given in Table 1.

Table 1

Change in the mechanical properties of capron specimens after ozonization and polymerization with styrene (averages of 4 experiments)

Starting capron specimen	Starting capron specimen	Duration of ozonization	Same specimen after ozonization	Same specimen after ozonization	Same specimen after ozonization and polymerization with styrene (5 hr. at 80°)	Same specimen after ozonization and polymerization with styrene (5 hr. at 80°)
E	σ		E	σ	E	σ
733	779	2 min.	726	798	741	818
733	779	5 min.	774	856	740	814
824	728	10 min.	849	738	902	693
718	870	20 min.	787	864	858	714
718	870	1 hr.	570	682	601	658
718	870	3 hr.	686	544	672	603
824	728	6 hr.	667	571	556	525

Note. Here and in Table 2, E is elongation at break (%), σ is tensile strength (kg/cm^2).

* A. P. Zasechkina took part in the experimental portion.

As can be seen from Table 1, when the duration of ozonation is changed, the properties of the capron film change in such a way that the tensile strength and elongation at break decrease. However, brief ozonation for 10–20 min practically does not worsen the film’ s characteristics and even, on the contrary, leads to a certain increase in mechanical strength; only when the duration of ozonation is increased to 1 hour or more is a decrease in it observed.

It is interesting to note that if the specimens are heated for some time (5 h) after ozonation, the properties of the polymer change appreciably—the breaking strength and elongation decrease. After ozonation the films acquire the ability to liberate iodine from a potassium iodide solution, which indicates the presence of oxidizing agents in them.

After ozonation the film was placed in styrene and kept in the liquid monomer for 5 h at 80° in a nitrogen atmosphere. The film was then washed by boiling in benzene for 1 hour and then rinsed with cold benzene.

Films treated in the manner described were subjected to mechanical tests, as a result of which it was found that their mechanical strength is usually somewhat higher than that of the original films after brief ozonation, and differs practically little from the strength of the films after ozonation, as can be seen from Table 1. The maximum weight gain after polymerization did not exceed 20%.

Next, we carried out similar experiments with films prepared from the polyamide anid G-669, which is a copolymer obtained from ϵ-caprolactam, hexamethylenediammonium adipate, and hexamethylenediammonium azelate (^{3}). The results obtained are given in Table 2.

Table 2

Change in the mechanical properties of specimens of anid G-669 after ozonation and polymerization with styrene (averages of 4 experiments)

Initial specimen of anid G-669: E	Initial specimen of anid G-669: σ	Duration of ozonation*	Same specimen after ozonation: E	Same specimen after ozonation: σ	Same specimen after ozonation and polymerization with styrene (5 h at 80°C): E	Same specimen after ozonation and polymerization with styrene (5 h at 80°C): σ
685	485	2 min.	768	472	648	470
454	400	10 min.	547	389	570	392
454	400	12 min.	534	425	651	425
454	400	15 min.	753	496	328	383
669	554	4 hours**	608	587	657	482
669	554	4 hours***	676	564	675	554
454	400	6 h	409	411	225	301

* Oxygen flow rate 80–85 ml/min.
** Maximum rate (140 ml/min.).
*** Minimum rate (40 ml/min.).

As can be seen from Table 2, in this case the same picture was observed as in the case of polycaprolactam.

Next, we measured the specific viscosities both of the initial polyamide specimens and of the same specimens after ozonation and polymerization. The data obtained are given in Table 3.

As can be seen from the data in Table 3, after ozonation an increase in the specific viscosity of the solution is observed. At the same time, an even more significant increase in the viscosity of the solution is observed after polymerization of the ozonized polyamide specimen.

Table 4 gives elementary analyses of several graft copolymers.

Table 3

Change in the intrinsic viscosity (η_{sp}) of polyamide samples after ozonization and polymerization (averages of 4 experiments)

Film	Before ozonization	After ozonization, 2 min	After polymerization	After ozonization, 5 min	After polymerization	After ozonization, 3 hours	After polymerization	After ozonization, 5 hours	After polymerization
Capron	0.538	0.599	0.712	0.704	0.740	0.739	0.785	0.622	0.491
Anid G-669	0.465	–	–	0.549	0.635	–	–	0.637	0.771

Table 4

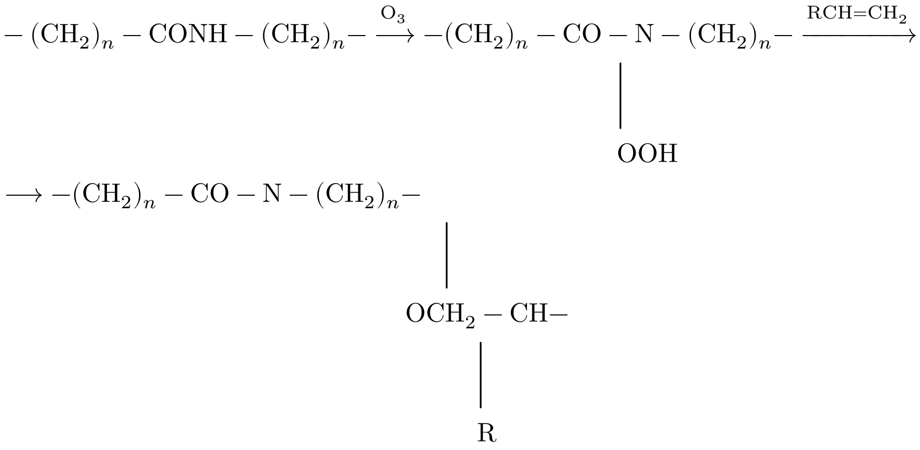
Change in the elemental composition of polyamide samples after ozonization and polymerization

Film	Before ozonization, calc., %	Before ozonization, found, %	After ozonization, 5 min, %	After polymerization, %	Graft, % of initial (avg.)	After ozonization, 5 hours, %	After polymerization, %	Graft, % of initial (avg.)
Capron	C 63.11H 10.60N 12.27	C 64.03H 9.64N 12.18	C 63.32H 9.80N 12.44	C 63.98H 9.64N 12.18	12.5	C 63.44H 9.64N 11.83	C 69.93H 9.14N 9.77	18.5
Anid G-669	C 64.96H 10.06N 11.65	C 63.91H 9.68N 11.16	C 64.53H 9.90N 12.09	C 65.63H 9.75N 11.05	8.3	C 64.26H 9.97N 11.57	C 70.86H 9.47N 9.56	21.12

We then carried out experiments on grafting methyl methacrylate to polyamides, which also gave the corresponding graft copolymers.

On the basis of the data obtained, it may be concluded that, as a result of the procedure we adopted, a layer of polystyrene or polymethyl methacrylate is formed which, apparently, is located on the surface of the polyamide film or fiber and is bound to it by chemical bonds. In this case, evidently, the formation of graft-copolymer molecules takes place predominantly in the surface layer of the polyamide: the grafted layer does not increase without limit—it does not exceed 20 wt. %. At the same time, the surface properties of the polyamide change, which is reflected in the deterioration of the wettability of the film by alcohol. The grafted polyamide Anid G-669 loses the ability to dissolve completely in alcohol. Its solubility in cresol and formamide also changes somewhat.

It may be thought that the reaction proceeds in the following manner:



$$-(\mathrm{CH_2})_n-\mathrm{CONH}-(\mathrm{CH_2})_n- \xrightarrow{O_3} -(\mathrm{CH_2})_n-\mathrm{CO}-\underset{\displaystyle \mathrm{OOH}}{\underset{|}{\mathrm{N}}}-(\mathrm{CH_2})_n- \xrightarrow{\mathrm{RCH{=}CH_2}}$$

$$\longrightarrow -(\mathrm{CH_2})_n-\mathrm{CO}-\underset{\displaystyle \mathrm{OCH_2}-\underset{\displaystyle \mathrm{R}}{\underset{|}{\mathrm{CH}}}-}{\underset{|}{\mathrm{N}}}-(\mathrm{CH_2})_n-$$

Evidently, peroxide compounds are first formed at the amide groups of the polyamide, and then molecules of the vinyl monomer add to these peroxide groups.

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CITED LITERATURE

1. E. H. Immergut, H. Mark, *Makromol. Chem.*, **18**, 19, 322 (1956).
2. A. Chapiro, *J. Polym. Sci.*, **29**, 321 (1958).
3. V. V. Korshak, T. M. Frunze, DAN, **97**, 675 (1954).