Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Grafting of Monochlorotrifluoroethylene onto Polyethylene by Pre-irradiation Method

Yoneho Tabata[a]; Junichi Fujikawa[a]; Keichioshima[a]
[a] Department of Nuclear, Engineering University of Tokyo, Tokyo, Japan

To cite this Article Tabata, Yoneho , Fujikawa, Junichi and Keichioshima(1971) 'Grafting of Monochlorotrifluoroethylene onto Polyethylene by Pre-irradiation Method', Journal of Macromolecular Science, Part A, 5: 5, 831 — 842
To link to this Article: DOI: 10.1080/00222337108061065
URL: http://dx.doi.org/10.1080/00222337108061065

J. MACROMOL. SCI.–CHEM., A5(5), pp. 831-842, August, 1971

Grafting of Monochlorotrifluoroethylene onto Polyethylene by Pre-irradiation Method

YONEHO TABATA, JUNICHI FUJIKAWA, and KEICHI OSHIMA

Department of Nuclear Engineering
University of Tokyo
Tokyo, Japan

SUMMARY

Radiation-induced grafting of monochlorotrifluoroethylene onto polyethylene was carried out by a pre-irradiation method. It was observed that the grafting proceeds rapidly at temperatures from -35 to 0°C in the liquid monomer phase. By measuring ESR spectra, it was found that the grafting can be initiated by allyl radicals trapped in polyethylene. An absorption band characteristic to the grafting site was found and the band was tentatively assigned to the stretching vibration of the C-F bond situated in the vicinity of the branching position (the initiating site).

INTRODUCTION

The grafting of tetrafluoroethylene onto polyethylene was reported in previous papers [1, 2]. We tried to graft monochlorotrifluoroethylene onto polyethylene and have succeeded in making a graft copolymer.

These results are described in this paper.

EXPERIMENTAL

Monochlorotrifluoroethylene was prepared by the dechlorination of trichlorotrifluoroethane in ethyl alcohol at 70°C with Zn powder as the catalyst.

$$CF_2Cl\,CFCl_2 + Zn \longrightarrow CF_2{=}CFCl + ZnCl_2$$

Monomers were washed with water and then dried with $CaCl_2$. Purity of the monomers was 99.99%.

Grafting and measurements of ESR were made in the same way as those described in the previous papers [1, 2].

RESULTS AND DISCUSSION

After Takathene (polyethylene polymerized in the vapor phase by radiation at Takasaki Radiation Research Establishment) was irradiated in an ampoule at -78°C under vacuum, monomers were introduced into the ampoule. Melting and solidification of the monomers in the ampoule was done repeatedly between -78 and -196°C, degassing was done, and grafting was carried out at -35 and 0°C. The results are shown in Fig. 1.

The grafting yield increases linearly with reaction time until the yield reaches a saturation value. Saturation in the yield was always observed at various grafting temperatures for various pre-irradiation doses. The temperature dependence of grafting may be due to the influence of temperature on the propagation reaction.

The saturation phenomenon may be due to the prevention of diffusion of monomers into the polyethylene matrix by the polymonochlorotrifluoroethylene formed in the early stage of grafting. Such phenomena have been observed in several other systems.

In the radiation-induced homopolymerization of monochlorotrifluoroethylene there is no acceleration phenomenon in the conversion curve and the rate of polymerization is proportional to the 0.5~0.6 power. The fact that there is no acceleration phenomenon in the homopolymerization seems to support the argument of diffusion control in the grafting process as mentioned above.

In other words, the grafting of the monomers onto polyethylene may be strongly influenced by the rate of diffusion of the monomers, and a

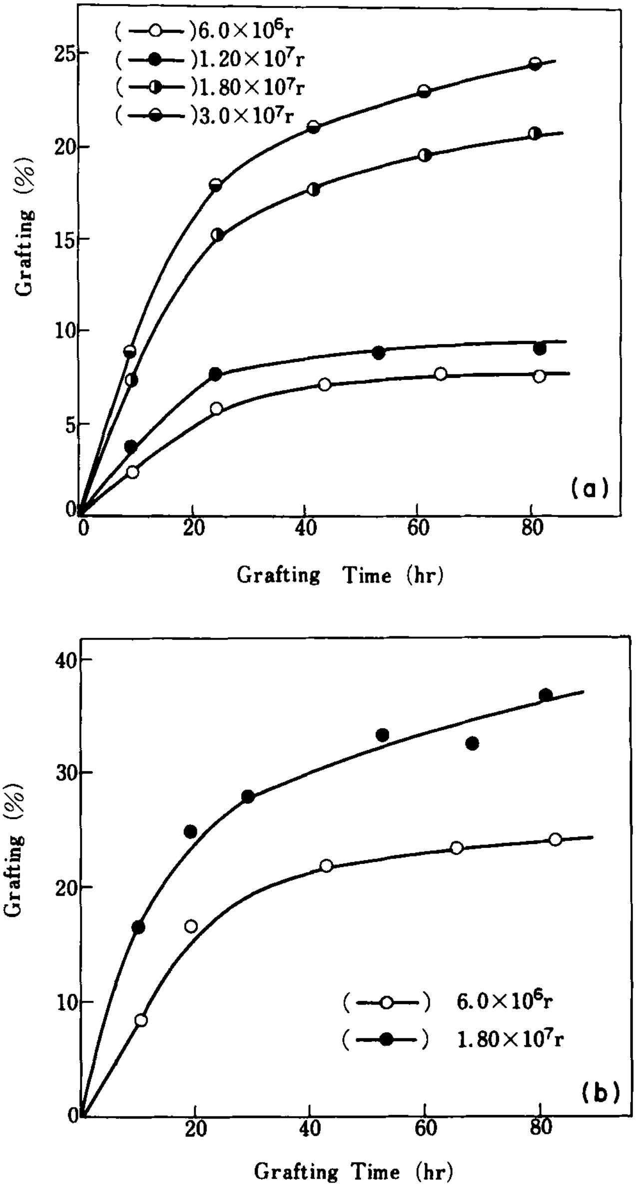

Fig. 1. Relations between grafting % and grafting time for various pre-irradiation doses. Pre-irradiation was carried out in a dose rate of 3.0 × 10^5 R/hr at -78°C. Grafting was made at -35°C (a) and 0°C (b).

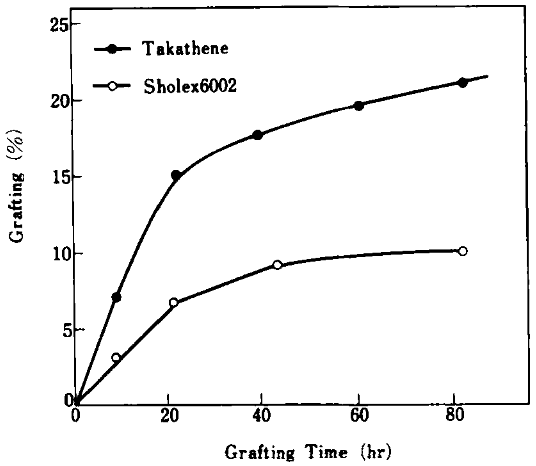

Fig. 2. Relations between grafting % and grafting time for two different polyethylenes. Pre-irradiation was carried out in a dose rate of 3.0 X 10^5 R/hr at -78°C for 60 hr and the grafting was made at -35°C.

saturation in the yield should be observed for a low rate of diffusion in the later stage of grafting. The grafting of Takathene and Sholex 6002 was compared. The results are shown in Fig. 2. As is obvious from the figure, the rate of grafting in Takathene is faster than that in Sholex 6002 by a factor of 2. The saturation phenomena are also observed in both polymers. On the other hand, in the case of grafting of tetrafluoroethylene onto polyethylene, there was an extremely large difference between the two polymers. This seems to be due to the difference in the reaction sites between tetrafluoroethylene and monochlorotrifluoroethylene.

ESR measurements during grafting have been made. After Takathene was irradiated with a dose of 1.80 X 10^7 R at -78°C under vacuum, monomer was introduced into the capillary. ESR measurements have been made in both the presence and absence of monomers. The spectra are shown in Fig. 3. The ESR measured at -78°C before the introduction of monomers into the capillary is shown in Fig. 3a. The spectrum changes from Fig. 3a to Fig. 3b were caused by introducing the monomers.

The difference between Fig. 3a and Fig. 3b spectra was obtained as shown in Fig. 4. This corresponds well to that of the allyl radical. This means that allyl radicals are consumed very rapidly by when the monomers are introduced and that the grafting reaction can be initiated by allyl radicals. Since about 30% of the radicals included in polyethylene irradiated in a dose of

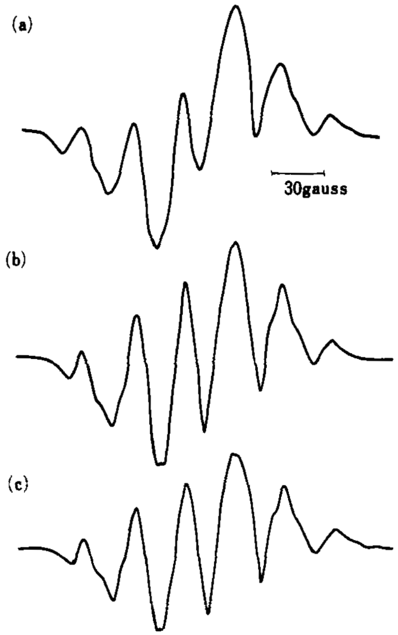

Fig. 3. Electron spin resonance spectra of irradiated polyethylene samples before and after grafting. Takathene was irradiated at -78°C in a dose of 1.80×10^7 R under vacuum. (a) Measured at -78°C without monomers. (b) Measured at -35°C, 10 min after the introduction of monomers. (c) Measured at -35°C, 40 hr after the introduction of monomers.

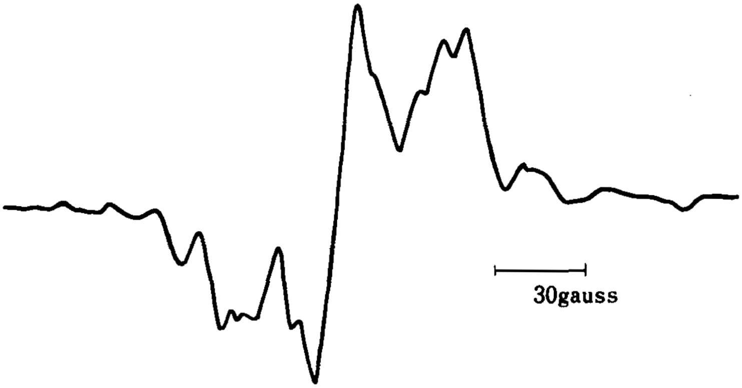

Fig. 4. Spectrum obtained from the difference of (a) and (b) in Fig. 3.

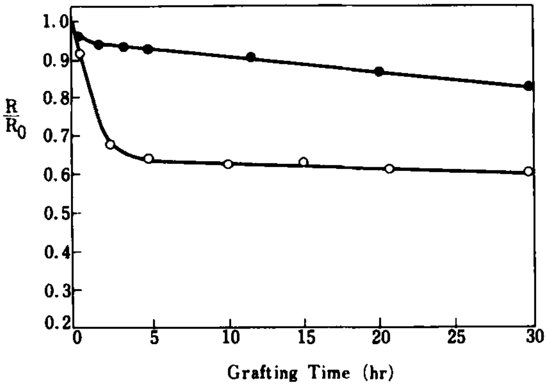

Fig. 5. Decay curves of polyethylene radicals in absence and presence of monomers. Relative concentration of radicals R/R_0 as a function of time. Pre-irradiation was made at -78°C in a total dose of 1.80×10^7 R. (●) Under vacuum, (○) in the presence of monomers.

about 10 Mrads at -78°C are of the allyl type, almost all allyl radicals are considered to participate in the initiation reaction in a short time (within about 2 hr). Decay of alkyl radicals does not relate to grafting under the experimental conditions.

The decay curves of the trapped radicals are shown in Fig. 5. As is obvious from the figure, the decay is very rapid in the early stage and about 35% of the trapped radicals disappear very rapidly. After the rapid decay period, decay is very slow in comparison with that in the absence of monomers.

In the presence of monomers, almost all allyl radicals are attacked very rapidly by the monomers, while in the absence of monomers, allyl radicals decay very slowly.

It was reported in the previous paper [2] that the grafting of tetrafluoroethylene onto polyethylene is mainly initiated by alkyl radicals. In the grafting of monochlorotrifluoroethylene onto polyethylene, however, the grafting is mainly initiated by allyl radicals, as in the many other cases.

To confirm that the initiating radicals are of the allyl type, the following experiments were made. After Marlex 15 was irradiated at a dose of 2.0×10^7 R, the irradiated polyethylene was kept at room temperature under vacuum for a week. The typical allyl radicals appeared and the spectrum is shown in Fig. 6a.

The concentration of the radicals decreased when monomers were

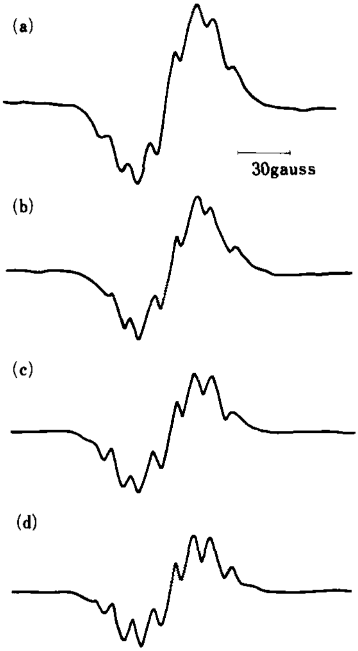

Fig. 6. Decay of allyl radicals by grafting. Marlex 15 was irradiated with a total dose of 2.0 × 10^7 R and the irradiated polymer was kept for 1 week at room temperature. (a) Spectrum of allyl radicals before introduction of monomers. (b) Further measurements were made 10 min (b), 20 hr (c), and 40 hr (d) after the introduction of monomers.

introduced into the capillary (Figs. 6a and 6b). After 10 min the concentration decreased about 20%. After 40 hr, a half of the initial concentration decayed. As is obvious from the results, the allyl radical concentration may decrease by being consumed in the initiation reaction of grafting. On the other hand, the spectrum becomes sharper during the decrease of the radical concentration.

From these results it may be concluded that the grafting of monochlorotrifluoroethylene onto polyethylene is initiated by allyl radicals, and the allyl radicals in the amorphous phase may be more reactive than those in the crystalline region.

To determine the effect of pre-irradiation temperature on the grafting it is also important to know the grafting mechanism. The results are shown in Fig. 7.

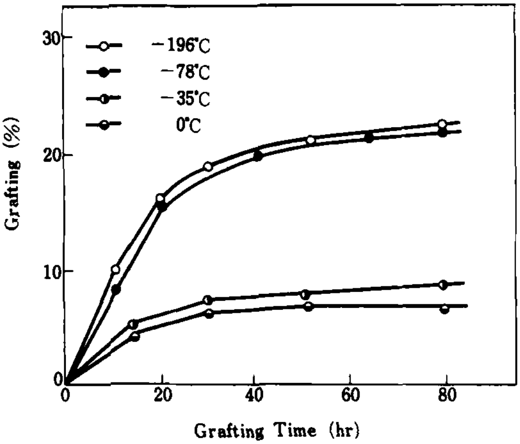

Fig. 7. Effect of pre-irradiation temperature on grafting at -35°C. The irradiation dose was 1.80 X 10^7 R at a dose rate of 3.0 X 10^5 R/hr. Grafting % as a function of grafting time at various pre-irradiation temperatures.

It is interesting to compare the grafting between the two different pre-irradiation temperatures -78 and -196°C. It is evident that there is actually no difference between the two. In the case of tetrafluoroethylen–polyethylene, there was a very large difference between the two. These results can explain without any contradiction that the initiating species in the former case corresponds to the allyl radical and that the latter case corresponds to the alkyl radical because allyl radicals are comparatively stable at relatively high temperatures and there is no large difference in the amounts of allyl radicals produced at different irradiation temperatures, such as -78 and -196°C.

On the other hand, at pre-irradiation temperatures of 35 and 0°C the grafting rate and the saturation yield decreased from those at -78 and -196°C. This may be due to retardation of the diffusion of monomers into polymers because, above the glass transition temperature of polymers (ca. -40°C), cross-linking occurs easily and the rate of diffusion should be decreased. Furthermore, the decay of allyl radicals also takes place to some extent above the glass transition temperature during irradiation.

The effect of the pre-irradiation dose on grafting may also give important information about the grafting mechanism. The relations between the initial rate of grafting and the pre-irradiation dose for two different grafting temperatures are shown in Fig. 8. It is evident from the experiments

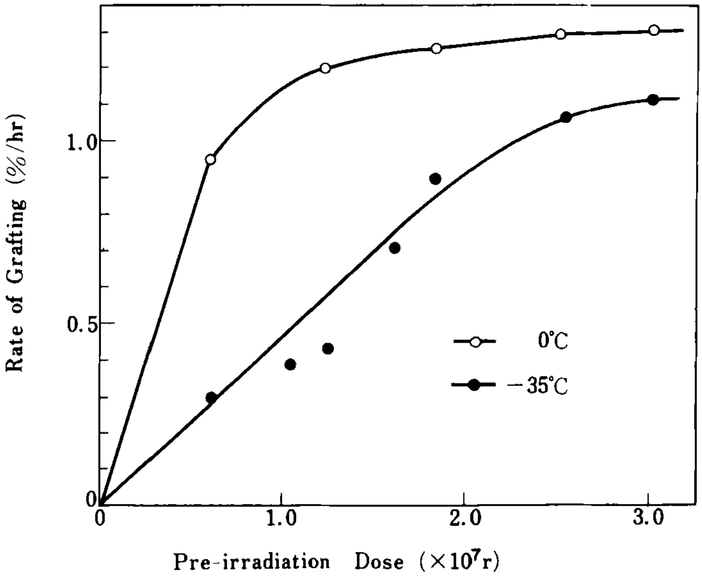

Fig. 8. Effect of pre-irradiation dose in grafting. Pre-irradiation was carried out at -78°C at a dose rate of 3.0 × 10^5 R/hr. Rate of grafting as a function of pre-irradiation dose at 0°C and -35°C.

that the rate of grafting approaches a constant value when the pre-irradiation dose increases for both grafting temperatures. Since the radical concentration is considered to increase linearly with the pre-irradiation doses, saturation in the grafting rate may not be due to the saturation of the radical concentration in polymers but be due to the change of the diffusion of monomers as a function of pre-irradiation dose.

Retardation in the diffusion of monomers may be expected because of the formation of cross-links or of grafted polymonochlorotrifluoroethylene. Since we are concerned about the initial rate of grafting, retardation in the diffusion of monomers may not be due to the formation of grafted polymers but to the formation of cross-links in the polymers. Above -40°C the G value of cross-linking increases with temperature, therefore both the grafting rate and the rate of cross-link formation are higher at 0°C than at -35°C. The rate of grafting therefore reaches saturation at a lower pre-irradiation dose at 0°C than at -35°C.

IR spectra of Takathene, polymonochlorotrifluoroethylene, and grafted copolymers are shown in Fig. 9. It is clear from the spectra that in the

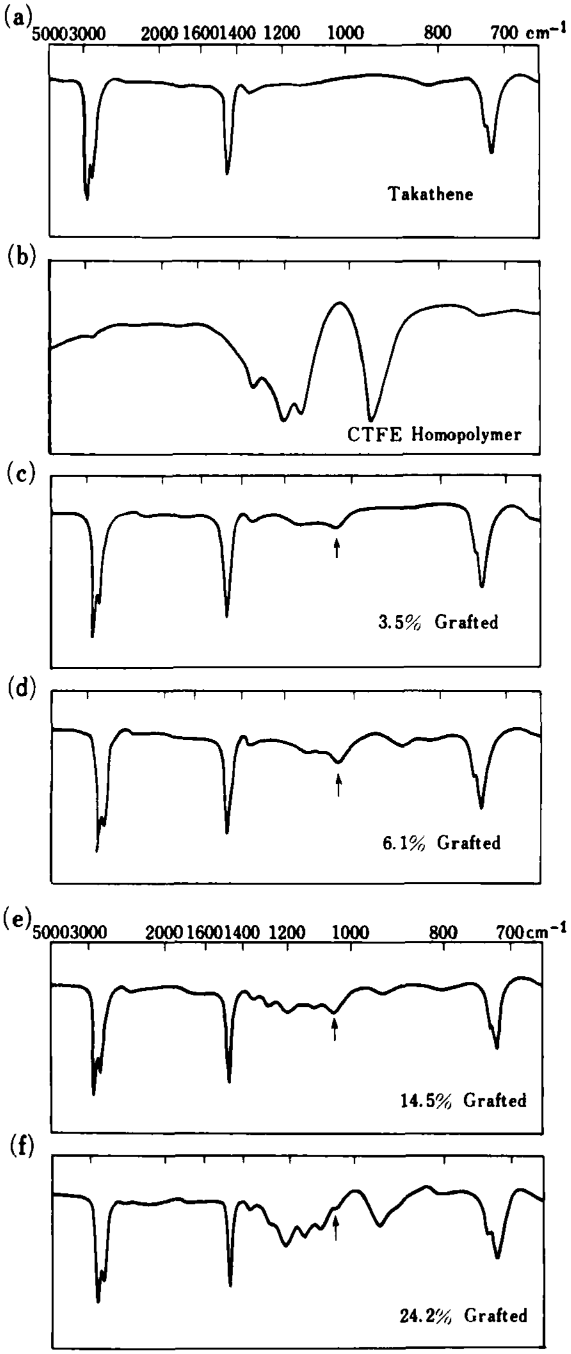

Fig. 9. Infrared spectra of both homopolymers and grafted copolymers at various grafting %.

grafted copolymers a characteristic absorption band at 1050 cm^{-1}, which cannot be found in the homopolymers, is observed. The intensity of the absorption band increases with the degree of grafting below about 10% grafting, as shown in the figure. For higher grafting yields the relative intensity of the characteristic band of the C–F stretching band of polymonochlorotrifluoroethylene is very low. The relative intensity decreases with the grafting % above about 10% grafting.

These results suggest that, up to 10% grafting, the initiation reaction takes place as does the propagation reaction of growing radicals. Above 10% grafting only the propagation reaction occurs.

The absorption at 1050 cm^{-1} may be due to the structure closely connected to the branching position. The absorption band may correspond to a vibration of the C–F band where it is situated in the vicinity of the branching position.

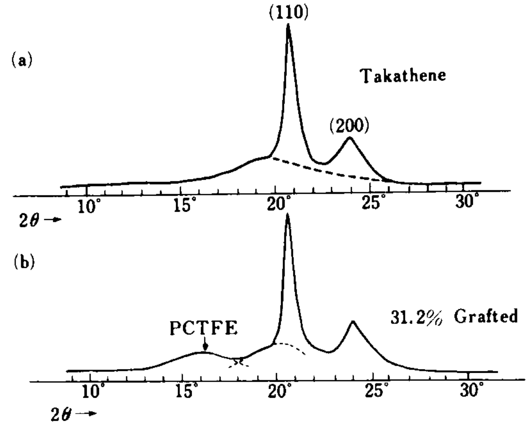

Fig. 10. X-Ray diffraction patterns of (a) Takathene and (b) 31.2% grafted Takathene.

X-Ray diffractions of Takathene and the grafted copolymer were measured. The results are shown in Fig. 10. Two main crystalline peaks at $2\theta = 21.7^\circ$, $2\theta = 23.8^\circ$, and a halo peak at $2\theta = 19^\circ$ are shown in Fig. 10a. For a 31.2% grafted copolymer, another halo peak at $\theta = 16^\circ$ appeared. From these results it can be stated that the grafted polymers are in an amorphous state, in contrast to the grafted polytetrafluoroethylene. There was no significant change in the amount of the crystalline part of Takathene before and after grafting. These results indicate that grafting proceeds mainly in the amorphous region of polyethylene.

CONCLUSIONS

Grafting of monochlorotrifluoroethylene onto polyethylene has been clearly shown in this paper. A saturation phenomenon in the grafting yield was observed and the saturation value had a maximum of about 30%. ESR measurements confirmed that the grafting can be initiated by allyl radicals formed in polyethylene by γ-irradiation. It was found that the branching point can be detected directly by IR absorption measurements in the monochlorotrifluoroethylene–polyethylene system. Finally, it was concluded by X-ray diffraction measurements that the grafted copolymers are in an amorphous state and that grafting proceeds mainly in the amorphous phase of polyethylene.

REFERENCES

[1] Y. Tabata, J. Fujikawa, S. Shu, and K. Oshima, *J. Macro. Sci.–Chem.*, **A5**, 793 (1971).
[2] Y. Tabata and J. Fujikawa, *J. Macro. Sci.–Chem.*, **A5**, 821 (1971).
[3] A. I. Kurilenko, E. P. Danilov, V. L. Karpov, *Vysokomol. Soedin.*, **9**, 2362 (1967).

Accepted by editor November 10, 1970
Received for publication January 13, 1971