Studies on Reactions of Polypropylene. V. On the Thermal Degradation Accelerated by Vinyl Polymers

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A few drawbacks are encountered in the use of polypropylene, for example, the poor flow properties resulting from its very high molecular weight and the poor dyeability resulting from its nonpolarity and high crystallinity. The former drawback has been solved either by the improvement of the polymerization process,[1-3] in which the molecular weight of polypropylene can be controlled, or by the degradation of polypropylene in order to reduce its very high molecular weight.[4-9]

As for the latter drawback, the modification of polypropylene has been much studied: graft polymers have been prepared,[10-15] dyeable polymers have been blended,[16-18] and some functional groups have been introduced to the polypropylene chain.[19,20] Also, two thermally degradative methods have been proposed for the modification of polypropylene: the thermal degradation of polypropylene in the presence of vinyl monomers,[21] and the thermal treatment of polypropylene containing 5—95% specified polymers.[22]

For this paper, the thermal degradation of polypropylene accelerated by vinyl polymers was studied in an attempt to overcome the drawbacks described above. The fundamental idea of this study was as follows: A vinyl polymer generally degrades easily to a monomer by the chain reaction mechanism,[23] but polypropylene degrades by the random scission mechanism.[4,5] As a vinyl polymer is more susceptible to thermal degradation than polypropylene, if the mixture of polypropylene and a vinyl polymer is heated at an elevated temperature, the active radical generated by the scission of a vinyl polymer chain may be effective as an accelerator in the degradation of polypropylene and the modification of polypropylene may be expected because of the interaction among a vinyl monomer, a vinyl polymer radical, a polypropylene radical and a polypropylene molecule. The vinyl polymers used in this study were polystyrene, polymethyl methacrylate, the 2-methyl-5-vinylpyridine - styrene copolymer, and the acrylonitrile - styrene copolymer. As had been expected, it was proved that the vinyl polymers added were effective not only in accelerating the thermal degradation of polypropylene, but also in forming graft or block polymers.

Experimental

Polypropylene. — Polypropylene (PP) was polymerized at 80°C in *n*-heptane by a catalyst consisting of titanium trichloride, dicyclopentadienyl titanium dichloride, sodium and hydrogen.[24] Polypropylene thus obtained was soaked in an excess methanol-isopropanol mixture (1:1) overnight after it had been separated from hot *n*-heptane under a nitrogen atmosphere, then it was filtered, washed with methanol, and soaked in methanol - concentrated hydrochloric acid mixture (10:1) overnight. Then polypropylene was

TABLE I. THE PROPERTIES OF POLYPROPYLENE

Sample	Intrinsic viscosity* dl./g.	Ash content %	Specific gravity**	Grain size mesh
PP(A)	6.60	0.03	0.914	60>
PP(B)	9.1	0.02	0.913	30>
PP(C)	4.75	0.02	0.913	30>
PP(D)	5.78	0.05	0.913	30>

* Values in tetraline at 135°C.

** Values at 23°C.

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1) E. J. Vandenberg, Japanese Pat. 495 (1960).

2) E. Bua and L. Luciani, Japanese Pat. 3192 (1961).

3) J. M. Kelley Jr., and J. R. Lovett, Japanese Pat. 15541 (1961).

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14) M. Lazar, R. Rado and J. Pavlinec, *J. Polymer Sci.*, **53**, 163 (1961).

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16) P. Ginstiniani, G. Natta and G. Mazzanti, U. S. Pat. 3115478.

17) U. Riboni and L. Bartolucci, U. S. Pat. 3116966.

18) T. Tanekoda, K. Akamatsu, T. Okamoto and K. Matsui, Japanese Pat. 26284 (1963).

19) K. S. Minsker, I. Z. Shapiro and G. A. Razuvayev, *Polymer Sci. U. S. S. R.*, **4**, 1 (1963).

20) S. Morimoto, O. Ishiwari and S. Uchida, Japanese Pat. 4683; 4733 (1963).

21) M. Watanabe and Y. Arata, Japanese Pat. 18392 (1962).

22) H. W. Coover, Jr., M. A. McCall and J. E. Guillet, U. S. Pat. 3121070; Japanese Pat. 5593 (1962).

23) H. H. G. Jellinek, "The Degradation of Vinyl Polymers," Academic Press Inc., Publishers, New York (1955), p. 68.

24) K. Azuma and K. Takahashi, Japanese Pat. 12141 (1962).

filtered, washed with a methanol-water mixture (10:1) and methanol, and dried under a vacuum. Polypropylene used contained no stabilizer. The properties are shown in Table I.

The Preparation of Samples.—The vinyl polymers used were polystyrene [PSt; intrinsic viscosity in a benzene solution at 25°C : 1.05 dl./g.], polymethyl methacrylate [PMMA; intrinsic viscosity in an acetone solution at 25°C : 1.22 dl./g.], and the 2-methyl 5-vinylpyridine - styrene copolymer [P(MVP-St); (2-methyl-5-vinylpyridine/styrene) in the copolymer : 1.2 by weight], and the acrylonitrile-styrene copolymer [P(A-St); (acrylonitrile/styrene) in the copolymer : 1.4 by weight]. All the vinyl polymers used were purified by reprecipitation.

The samples were prepared as follows: PP powder was stirred into a PMMA-acetone solution, a P(MVP-St)-acetone solution, a P(A-St)-acetone solution or a PSt-toluene solution. In the case of the acetone solution, the acetone was evaporated by stirring under a vacuum. The slurry of PP powder and the PSt-toluene solution was poured into excess methanol in a mixer. The polymer precipitated was filtered, washed with methanol and dried under a vacuum. The quantity of PSt, PMMA, and P(MVP-St) added to polypropylene was regulated at 3% by weight, while the quantity of P(A-St) was 4.7% by weight.

The Viscosity Measurements and the Calculation of the Scission Number.—The viscosity of the tetraline solution of the polymer sample containing 0.2 g. of 2, 6-di-*t*-butyl *p*-cresol per 100 ml. of tetralin was determined at 135°C with an Ubbelohde viscometer under a nitrogen atmosphere. The intrinsic viscosity was determined from the three-point measurement by extrapolation. The scission number of the polypropylene chain (S) per molecule, with the molecular weight calculated by Parrini's equation[25] $[[\eta]=0.80\times10^{-4}\,\mathrm{M}^{0.80}]$, was calculated by the following equation:

$$S=(1/0.524)\{([\eta]_0/[\eta]_t)^{1/0.80}-1\}$$

$[\eta]_0$: The intrinsic viscosity of a sample before thermal degradation

$[\eta]_0$: The intrinsic viscosity of a sample after thermal degradation for t hr.

This equation was derived from Matsumoto's equation[26] and Parrini's equation,[25] and it was previously applied to the analysis of the thermal degradation of polypropylene by Oshika.[9]

Thermal Degradation in a Glass Ampoule.—The sample (0.3 g.) was transferred into an ampoule of 6 mm. in diameter and 10 cm. in length. The ampoule was then evacuated by the use of an oil diffusion pump for one hour after three cycles of evacuation-nitrogen substitution. The ampoule was sealed off and dipped into a salt bath of sodium nitrate - potassium nitrate. The hot ampoule was rapidly cooled in water, and the viscosity of the polymer was determined.

Thermal Degradation by the Use of an Extruder. — The thermal degradation by the use of an extruder was studied under a nitrogen stream in order to consider the practical utility of the thermal degradation of polypropylene accelerated by vinyl polymers. Figure 1 gives a rough sketch of the extruder. The extruder was a modification of type MK-1 from Modern Machinery Co., Ltd., the heating zone of which was divided into three parts.

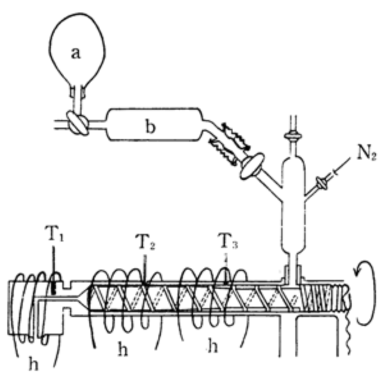

Fig. 1. The rough sketch of the extruder.
a : Nitrogen-balloon
b : Sample
T$_1$, T$_2$ and T$_3$: Thermo-couple
h : Heater

Volatilization Curves.—Volatilization curves of the samples were determined under a nitrogen stream with a differential thermal analysis apparatus DT-1A from Shimadzu Seisakusho, Ltd., in order to compare the thermal stability of the samples. The heating rate was 2°C/min.

The Acetone-Extraction of Degraded Samples.—The sample degraded by the use of the extruder was in the shape of a pellet. The sample was dissolved in *p*-xylene under a nitrogen atmosphere, and the hot solution was slowly cooled overnight, then the slurry obtained was poured into methanol [for the PP(A)-PSt sample, the PP(A)-PMMA sample, and the PP(D)-P(A-St) sample] or petroleum ether [for the PP(D)-P(MVP-St) sample] in a mixer. The precipitate was filtered, washed with methanol or petroleum ether, and dried under a vacuum. The powder obtained was extracted by acetone[12] with a Soxhlet extractor for 20 hr. under a nitrogen atmosphere. The residue was dried under a vacuum, and the vinyl polymer content of the residue was determined by infrared spectrum analysis, using a spectrophotometer, type AR-275, from Shimadzu Seisakusho Co., Ltd. The determination was carried out by the base-line method[27] using the following analytical wavelengths: PSt 14.4 μ, PMMA 5.8μ, and PMVP 13.6 μ.

Results and Discussion

Volatilization Curves.—Figures 2 and 3 show the volatilization curves of the PP(C), PP(D), PSt, PMMA, P(A-St), P(MVP-St), PP(C)-PSt, PP(C)-PMMA, PP(D)-P(A-St), and PP(D)-P(MVP-St)

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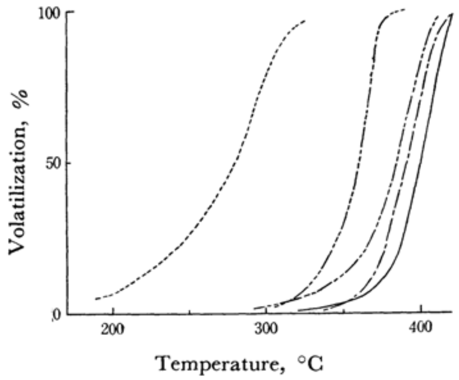

Fig. 2. Volatilization curves.
——: PP(C), —–—: PSt, ----: PMMA,
—-—: PP(C)-PSt, —--—: PP(C)-PMMA

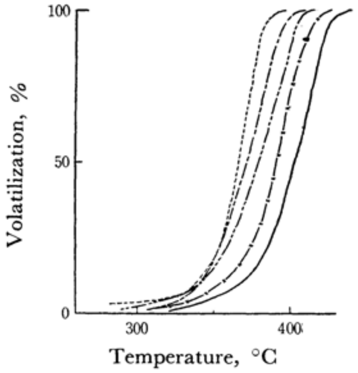

Fig. 3. Volatilization curves.
——: PP(D), —–—: P(MVP-St),
----: P(A-St), —×—: PP(D)-P(MVP-St),
—--—: PP(D)-P(A-St)

samples. The volatilization curves of the PP(C)-PSt, PP(C)-PMMA, PP(D)-P(A-St), and PP(D)-P(MVP-St) samples were between the volatilization curves of PP(C) or PP(D) and those of PSt, PMMA, P(A-St), and P(MVP-St) respectively. These relations of the volatilization curves may be considered as suggesting the accelerating effect of vinyl polymers for the thermal degradation of polypropylene.

Thermal Degradation in a Glass Ampoule. —Figures 4—9 show the changes in the relative intrinsic viscosity with the reaction time at 280—345°C. Apparently, the changes in the relative intrinsic viscosity of the PP(A)-PSt, PP(A)-PMMA, PP(D)-P(A-St), and PP(D)-P(MVP-St) samples were larger than those of PP(A) and PP(D). Figures 10—15 show the changes in the scission number of the polypropylene chain with the reaction time, but it is necessary to note that the effect of addition of the vinyl ploymers was neglected. The scission rate was constant at a definite temperature, and the vinyl polymers were proved to be effective as accelerators for the thermal degradation of polypropylene. Judging from the fact that

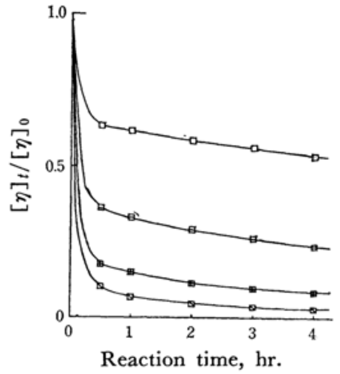

Fig. 4. The change in relative intrinsic viscosity of PP(A) with reaction time at various temperatures.
Reaction temperature;
-□-: 280°C, -⊟-: 300°C
-⊞-: 320°C, -⧅-: 340°C

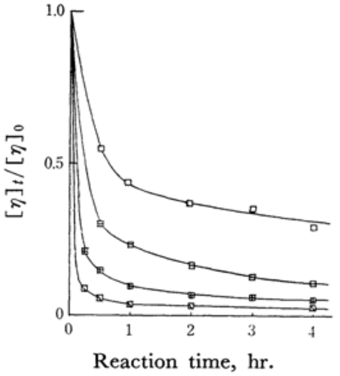

Fig. 5. The change in relative intrinsic viscosity of PP(A)-PMMA sample with reaction time at various temperatures.
Reaction temperature;
-□-: 280°C, -⊟-: 300°C
-⊞-: 320°C, -⧅-: 340°C

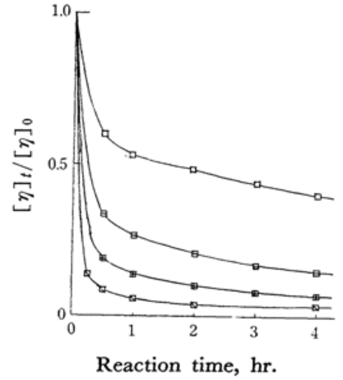

Fig. 6. The change in relative intrinsic viscosity of PP(A)-PSt sample with reaction time at various temperatures.
Reation temperatures;
-□-: 280°C, -⊟-: 300°C
-⊞-: 320°C, -⧅-: 340°C

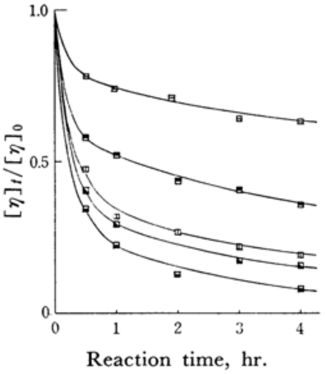

Fig. 7. The change in relative intrinsic viscosity of PP(D) with reaction time at various temperatures.

Reaction temperature;

-⊟-: 300°C, -⬒- 315°C, -◫- 330°C
-◪-: 334°C, -⬓- 345°C

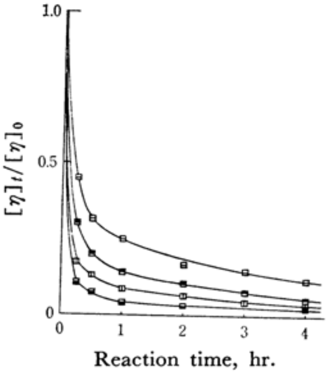

Fig. 8. The change in relative intrinsic viscosity of PP(D)-P(MVP-St) sample with reaction time at various temperatures.

Reaction temperature;

-⊟-: 300°C, -⬒-: 315°C
-◫-: 330°C, -⬓-: 345°C

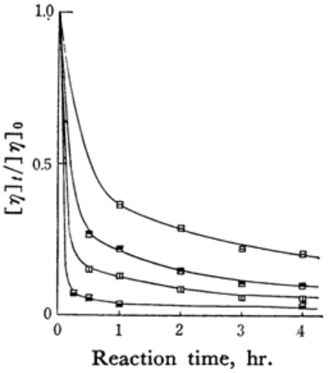

Fig. 9. The change in relative intrinsic viscosity of PP(D)-P(A-St) sample with reaction time at various temperatures.

Reaction temperature;

-⊟-: 300°C, -⬒-: 315°C
-◫-: 330°C, -⬓-: 345°C

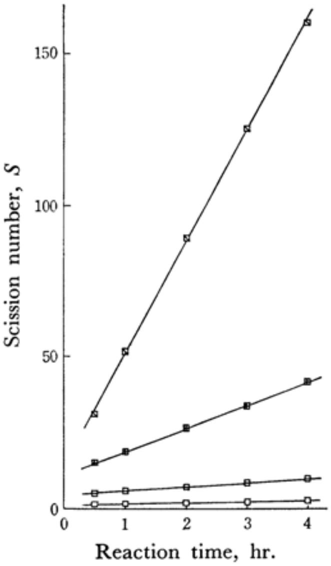

Fig. 10. Scission number of PP(A) vs. reaction time.

Reaction temperature;

-□-: 280°C, -⊟-: 300°C
-⊞-: 320°C, -⧅-: 340°C

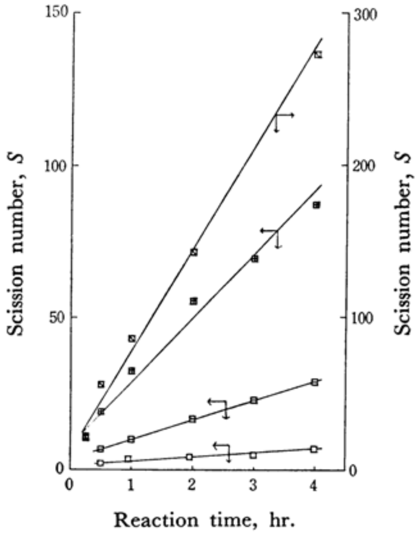

Fig. 11. Scission number of PP(A)-PMMA sample vs. reaction time.

Reaction temperature;

-□-: 280°C, -⊟-: 300°C
-⊞-: 320°C, -⧅-: 340°C

the straight lines in Figs. 10—15 did not pass the origins, the scission rate at the initial step of the reaction should be larger than that at the stationary step of the reaction, and this should be attributed to the weak bond in the polymers.[5,9)

Figure 16 shows a plot of the logarithm of the scission rate versus the reciprocal of the absolute

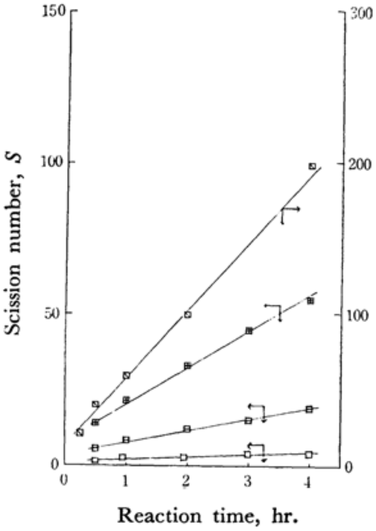

Fig. 12. Scission number of PP(A)-PSt sample vs. reaction time.
Reaction temperature;
-□-: 280°C, -⊟-: 300°C
-⊞-: 320°C, -⧅-: 340°C

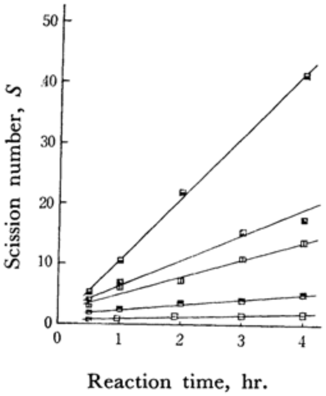

Fig. 13. Scission number of PP(D) vs. reaction time.
Reaction temperature;
-⊟-: 300°C, -⬒-: 315°C, -◫-: 330°C,
-◩-: 334°C, -⬓-: 345°C

temperature, and the response to the Arrehenius law is considered to be good. From the gradient of the straight line as determined by the method of the least squares, the activation energies for the scission reaction of the samples were calculated to be as follows:

57.2 kcal./mol. for PP(A),
58.4 kcal./mol. for PP(D),
46.8 kcal./mol. for the PP(A)-PSt sample,
43.5 kcal./mol. for the PP(A)-PMMA sample,
46.9 kcal./mol. for the PP(D)-P(A-St) sample,

and 38.6 kcal./mol. for the PP(D)-P(MVP-St) sample.

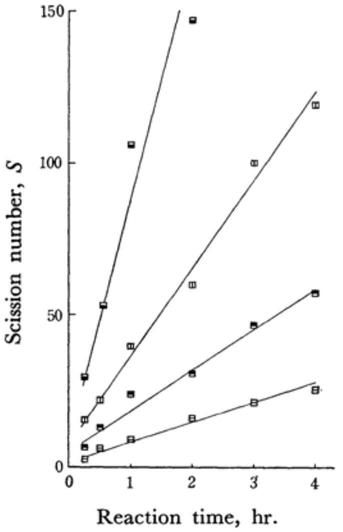

Fig. 14. Scission number of PP(D)-P(MVP-St) sample vs. reaction time.
Reaction temperature;
-⊟-: 300°C, -⬒-: 315°C
-◫-: 330°C, -⬓-: 345°C

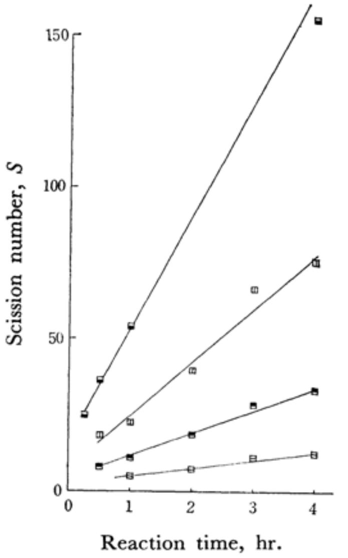

Fig. 15. Scission number of PP(D)-P(A-St) sample vs. reaction time.
Reaction temperature;
-⊟-: 300°C, -⬒-: 315°C
-◫-: 330°C, -⬓-: 345°C

The activation energies for PP(A) and PP(D) could be cosidered to be consistent, but the reason for the difference between the scission rate of PP(A) and that of PP(D) is not clear. The values for PP(A) and PP(D) were larger than the value obtained by Hamada[5] (51.4 kcal./mol. at 250—320°C), while they were smaller than the value obtained by Davies et al.[4] (65 kcal./mol. at 250—300°C). The values for the PP-vinyl polymer

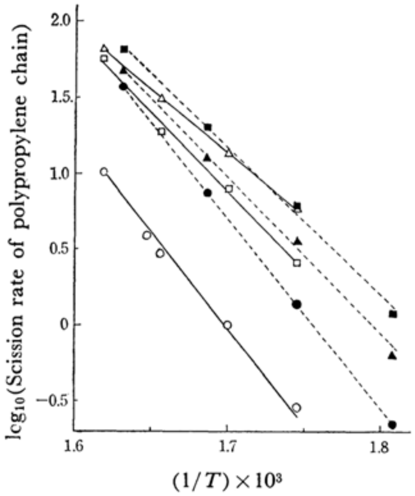

Fig. 16. log$_{10}$(Scssion rate of polypropylene chain) vs. (1/T).
--●--: PP(A), --▲--: PP(A)-PSt,
--■--: PP(A)-PMMA, -○-: PP(D),
-△-: PP(D)P(MVP-St), -□-: PP(D)-P(A-St)

samples were smaller than the values for PP(A) and PP(D). This difference may be attributed to the accelerating effect of the vinyl polymers added.

The orders of the activation energies of the PP(A) series or the PP(D) series were consistent with the order of thermal stabilities, as is shown in Figs. 2 and 3 respectively.

The value of the PP(D)-P(A-St) sample could not be compared with the values of the other PP-vinyl polymer samples, because of the difference in the quantity of the vinyl polymers added.

In this study, the degradation process was regarded as only the scission process of the polypropylene chain. However, as the formation of graft or block polymers was observed, as will be described later, such reactions as the degradations of a vinyl polymer chain and of a polypropylene chain and the interaction among a vinyl monomer liberated by the thermal degradation, a vinyl polymer radical, a polypropylene radical, and a polypropylene molecule must be considered simultaneously. The study of these reactions would be an interesting theme in the future.

Thermal Degradation by the Use of an Extruder and Acetone-Extraction.—Table II shows the results of the thermal degradation of PP(C)-PMMA and PP(D)-P(MVP-St) samples by the use of an extruder. The accelerating effect of PMMA and P(MVP-St) may easily be observed from Table II. When these results are compared with those of the thermal degradation in the glass ampoule, it is clear that the reaction time needed here for modification to the appropriate intrinsic viscosity of polypropylene by the use of the extruder is shorter than that in the glass ampoule. As plausible reasons for this difference, the following factors may be listed: the mechanical shearing effect of the extruder, the mechanical mixing effect of the extruder, and the effect of a trace of oxygen which could not be eliminated because of the imperfect airtightness of the extruder.

Regarding the mechanical shearing effect, it was well known that the mechanical degradation process has a negative temperature coefficient, since the bulk viscosity decreases and since, therefore, the degradative effect of the mechanical shear is reduced at higher temperatures until it finally become negligible. For example, the mechanical shearing effect is negligible for natural rubber at about 120°C.[28] In order to judge whether the mechanical shearing effect was negligible or not, PP([η]: 4.30 dl./g., specific gravity: 0.911) was extruded in a nitrogen atmosphere under these conditions: T$_1$: 190°C, T$_2$: 240°C, T$_3$: 200°C, and

TABLE II. THE RESULT OF THE THERMAL DEGRADATION BY THE USE OF THE EXTRUDER

Sample	Quantity of vinyl polymer added %	Thermal degradative conditions				Intrinsic viscosity dl./g.
		Temp. of the extruder, °C			Rotation speed of screwing shaft round/min.	
		T_1	T_2	T_3		
PP(B)-PMMA	0	220	340	330	7*	3.15
	1	220	340	280	30***	1.60
	1	220	320	280	30	2.90
	3	220	320	280	30	2.15
	5	220	320	280	30	1.95
	5	220	320	280	20**	1.46
PP(D)-P(MVP-St)	0	200	330	275	20	2.75
	3	200	330	275	10	1.58
	3	200	330	275	20	1.64
	3	200	330	275	34	1.75

* The retention time of a sample in the extruder was about 8 min.
** The retention time of a sample in the extruder was about 3.5 min.
*** The retention time of a sample in the extruder was about 2.3 min.

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28) R. J. Ceresa, "Block and Graft Copolymers," Butterworths, London (1962), p. 69.

TABLE III. THE RESULT OF ACETONE EXTRACTION

Sample	Thermal degradation conditions				Quantity of vinyl polymer added %	Intrinsic viscosity dl./g.	Content of vinyl polymer in the residue after acetone-extraction %	$\frac{\text{Vinyl polymer in the residue}}{\text{Vinyl polymer added}}$
	Temp. of the extruder, °C			Rotation speed of screwing shaft				
	T_1	T_2	T_3	round/min.				
PP(C)-PMMA	220	340	320	30	3	1.79	0.23	0.08
PP(C)-PSt	220	335	315	35	3	1.75	1.47	0.49
PP(D)-(MVP-St)	200	330	275	10	3	1.58	0.50 {PMVP: 0.20 PSt: 0.30	0.17 {PMVP: 0.12 PSt: 0.22

rotation speed of the screwing shaft: 30 round/min. Since the thermal degradation under these conditions was found to be negligible and since no degradation was observed ([η] of PP extruded: 4.29 dl/g.), the mechanical shearing effect was judged to be negligible. Therefore, it is reasonable to say that the shearing effect was negligible for the degradation shown in Table II.

The effect of the trace of oxygen was negligible in the results described above, but this fact can not assure that the effect of the trace of oxygen is negligible for the degradation shown in Table II, as the temperature of the above experiment is considerably lower than that shown in Table II. Also, the mechanical mixing effect may be effective, because the diffusion of the active radicals generated in the viscous polymer phase will probably not be easy and so the mechanical mixing might be effective in promoting the diffusion and the reaction of active radicals.

Table III shows the results of acetone-extraction. The formation of graft or block polymers was confirmed from the fact that a considerable quantity of the vinyl polymers was detected in the residue after acetone-extraction, while, no vinyl polymer was detected in the residue from PP-P(MVP-St) and PP-PSt mixtures after acetone-extraction. Furthermore, the monomer unit ratio (MVP/St) in the residue from the PP(D)-P(MVP-St) sample was 0.67, smaller than that of P(MVP-St) itself (MVP/St=1.2). This interesting finding may be a key to a solution of the question of whether or not the vinyl polymers degrade to monomers in the thermal degradation process.

The thermal degradative process of the vinyl polymers to the monomers may, therefore, be considered to accelerate the polypropylene degradation. The details should be elucidated by a study using a fractionated vinyl copolymer with a narrow molecular weight distribution and a difinite monomer unit ratio.

Dyeability.—The fibers spun from the modified polymers showed a good dyeability by dispersed dyes, such as Celliton Blue Extra Type, Latyl Cerise B, and Diacelliton Fast Yellow G. It was established by the microscopic observation of the cross section of dyed fibers that the colored vinyl polymer was dispersed in the shape of a granule and that the dispersed state of the colored vinyl polymer in the modified polypropylene was finer and more preferable to that of polypropylene fibers blended only with the vinyl polymer. The graft or block polymers formed in the thermal degradation should play an important role in improving the dispersion state of the colored vinyl polymer in the modified polypropylene.

Summary

The thermal degradation of polypropylene in the presence of such vinyl polymers as polystyrene, polymethyl methacrylate, the 2-methyl-5-vinylpyridine-styrene copolymer, and the acrylonitrile-styrene copolymer has been studied at 280—345°C by the use of glass ampoules and an extruder.

1) The vinyl polymers added were effective as accelerators for the thermal degradation of polypropylene. The activation energies for the scission reaction of the polypropylene chain were 57.2 and 58.4 kcal./mol. for the two polypropylene samples, and 46.8, 43.5, 46.9 and 38.6 kcal./mol. for polypropylenes containing 3% polystyrene, 3% polymethyl methacrylate, 4.7% the acrylonitrile-styrene copolymer, and 3% the 2-methyl-5-vinylpyridine-styrene copolymer respectively.

2) The reaction time needed for the modification of polypropylene to an appropriate intrinsic viscosity by the use of an extruder is shorter than that in glass ampoules.

3) Graft or block polymers have been detected in the residue after the acetone-extraction of the extruded polypropylene. They could be used in the modification of the polypropylene dyeability.

4) It has been concluded that the simple process of the thermal degradation of polypropylene accelerated by vinyl polymers can be used for the modification of polypropylene with a very high molecular weight and, simultaneously, for the preparation of graft or block polymers.

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