



Reaction mechanism and rheological properties of polypropylene irradiated under various atmospheres

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Abstract

It is well-known that the melt-strength properties of a polymer increases with molecular weight and with long chain branching due to the increase in the entanglement level. This study is a contribution for the understanding of the following points: — the role of branching, crosslinking and degradation on melt strength properties; — the mechanism and the kinetics of PP irradiation with time of irradiation and the importance of double bond formation.

The results showed that degradation was the major reaction in the initial step of irradiation no matter the atmosphere and or antioxidant. However, double bond formation increased the production of branching and crosslinking reactions. Double bond formation had no effect on the crystallization kinetics, on the other hand, long chain branching had a marked effect on the crystallization temperature. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

PP suffers from low melt strength, i.e., the melted PP does not exhibit an increase in resistance to stretching during elongation. It is well-known that the melt-strength properties of a polymer increases with molecular weight and with long chain branching due to the increase in the entanglement level. The production of long-chain branching in PP by irradiation in oxygen

free atmosphere is already claimed (US Patent 4,916,198, 1990; US Patent 5,414,027, 1995). The irradiation of PP in the presence of polyfunctional monomers to improve the elongational viscosity was studied by Yoshi et al. (1986a). This study is a contribution for the understanding of the following points: — **The effect of radiolysis products on the kinetics of crystallization** — DSC studies on the effects of irradiation on PP have been performed when information about the changes in morphology are sought (Busfield and O'Donnell 1979; Avrami, 1940). Moreover, the nucleating effects of HMSPP (high melt strength polypropylene) alone or mixed with others polymers are well-known and the crystallization pro-

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Table 1
Melting and non-isothermal crystallization parameters^a

Dose (kGy)	Virgin PP plus Acetylene					Stabilized PP plus acetylene				
	t_m	t_c	(t_m-t_c)	ΔH_f	ΔH_c	t_m	t_c	(t_m-t_c)	ΔH_f	ΔH_c
0	–	–	–	–	–	440,5	390,4	50,1	30,8	38,5
10	437,2	389,5	47,7	28,7	43,3	440,3	390,7	49,6	30,4	39,2
20	436,5	389,3	47,2	28,4	43,2	439,1	391,7	47,4	29,6	38,6
40	433,1	390,1	43,0	31,8	41,0	438,1	391,8	46,3	30,4	37,7
60	431,6	392,2	39,4	32,4	39,6	434,5	391,0	43,5	31,4	36,3
80	429,2	394,9	34,3	35,6	39,6	434,0	390,7	43,3	30,3	35,0
100	427,2	396,1	31,1	33,7	35,3	433,1	389,8	43,3	30,6	34,3
150	422,1	395,1	27,0	32,0	31,1	428,8	388,3	40,5	31,0	29,8
200	421,0	393,6	27,4	30,4	31,1	425,2	385,8	39,4	31,5	30,1

^a Legend: t_m : melting temperature (K); t_c : crystallization temperature (K); ΔH_f : fusion enthalpy; ΔH_c : crystallization enthalpy.

cess was already used as an indirect way for monitoring the changes in melt strength. Thus, the investigation of the mechanism of HMSPP crystallization was important and isothermal and kinetics studies were never reported in the literature. **The role of branching and crosslinking on melt strength properties** — physical crosslinks or long chain branchings are considered the most beneficial molecular fixture for achieving the combination of melt strength and processing properties. This study proposed the investigation of the effect of chemical crosslinking in the system; **The mechanism of molecular changes in PP, mostly on the initial stage of irradiation** — many authors (Black and Lyons, 1957; Dole and Schnabel, 1963) already studied the vacuum irradiation of PP. The effect of acetylene and antioxidant was studied at low doses to check whether the kinetics of degradation and crosslinking would be constant over the range of irradiation.

2. Experimental

2.1. Materials and irradiation

Virgin polypropylene (vPP) and stabilized (sPP) produced by OPP Corporation, brand name H503, ($M_n=72,900$ and $M_w=380,800$) were irradiated with gamma (Co-60) and electron radiation in acetylene atmospheres followed by annealing. The atmospheres were (a) inert with N_2 , (b) chain transfer with H_2 and (c) crosslinking with acetylene. The samples were characterized as follow: SEC (WATERS 150C, detector IR and Viscotek mod150R; DSC 2910 TA; heating rate and cooling rate of $10^\circ C/min$; gel content by boiling 24 h in xylene; die swelling on INSTRON capillary rheometer, orifice of $0.03''$, and melt strength measured on a capilograph with orifice of 2.095 mm at 463 K, with acceleration of $6 cm/s^2$.

Table 2
Rate parameters and Avrami slope parameters on crystallization at 400 K^a

Dose γ (kGy)	Acetylene ($*10^{-2}$)				Hydrogen ($*10^{-2}$)				Nitrogen ($*10^{-2}$)			
	K_1	K_2	K_3	n	K_1	K_2	K_3	n	K_1	K_2	K_3	n
0	7.5	8.6	34	2,52	7.5	8.6	34	2,52	7.5	8.6	34	2,52
1	6.9	7.3	31	2,57	–	–	–	–	–	–	–	–
5	6.5	6.8	30	2,61	7.4	8.4	35	2,27	7.4	6.2	31	2,38
10	5.8	6.4	27	2,66	7.4	8.6	40	2,46	5.8	6.5	28	2,26
20	–	–	–	–	6.0	6.6	26	2,36	6.9	7.8	34	2,66
40	–	–	–	–	6.3	7.0	31	2,48	5.2	5.6	24	2,34

^a Legend: k_1 =Modified Avrami; k_2 =Reciprocal time to 50% completion; k_3 =Reciprocal time to 1% completion; n = Avrami slope parameter.

Table 3
Characteristics of PP irradiated in reducing and crosslinking atmosphere

No.	Irradiation dose (kGy); source (γ , e^-)	Atmosphere	Melt strength (cN); extensibility (cm s^{-1})	T_c (K)	T_{m2} (K)	Mn	Mw	Mz	M_w/M_n
1	0	–	10.3 at 9.0	387	436	72,900	380,800	1,274,000	5.2
2	3; e^-		387	433	51,000	245,700	765,400	4.8	
3	10; e^-	Acetylene		393	433 ^a	47,000	245,200	892,600	5.2
4	15; e^-			393	432 ^a	41,100	221,300	937,600	5.4
5	10; \bullet	Reducing		389	436	66,800	382,800	1,338,000	5.7
6	15; \bullet	plus	17.3 at 10.9	393	436	59,600	350,100	1,132,000	5.9
7	20; \bullet	acetylene	33.3 at 12.4	394	435 ^a	51,400	316,800	1,012,000	6.2
8	15; e^-			393	435 ^a	56,200	289,700	961,700	5.2

^a Broad melting peak, showing a pseudo-melting at around 416–420 K.

3. Results and discussion

DSC runs were taken to evaluate the effects of irradiation on morphology, on structural modifications and on nucleation. Table 2 shows the results of melting and crystallization for polypropylene non-stabilized (virgin) and stabilized both irradiated in acetylene. From the data on enthalpy of the first melt in Table 1, it is shown for both series that the crystalline content does not change upon irradiation. However, the melting temperature decreases steadily with dose and, after crystallization, the reformed crystallinity decreases with dose. The crystallization temperature increases slightly for the virgin PP and decreases at high doses for the stabilized PP. The higher decrease in the temperature of the first melting for the virgin PP can be associated with the defects caused by radiation in the interlamellar region, while in the stabilized sample this effect is reduced. The increase in crystallinity for both series is assumed to be caused by degradation at low doses. This observation supports the finding that the initial reactions of PP under irradiation is always degradation of strained molecules linking neighboring lamellae.

The rate parameters calculated for isothermal crystallization of polypropylene irradiated at various doses by gamma irradiation in different atmospheres are shown in Table 2. The rate parameters decrease as the irradiation dose increases for all tested atmosphere. This trend was especially marked for the series performed in acetylene, while the series in hydrogen and nitrogen show a less well-defined decrease. The PP irradiated with acetylene is assumed to have reacted in a clear crosslinking pattern over the degradation, on the other hand the N_2 and H_2 samples were supposed to be strongly degraded at low doses and crosslinked to a higher extent with increasing doses. Interestingly, the sample irradiated in H_2 showed an inverse trend at low doses, i.e., the rate parameter increase from 0 to 10 kGy and more remarkable was the very high value

of the reciprocal time k at 1% crystallization, evidence of a strong nucleation phenomena. One possible explanation was that the chain transfer character of H_2 worked in a degrading way, with no effect in preventing degradation as expected, but avoiding crosslinking due to lack of free radicals at the proper location. Probably the extensive double bond formation promoted a crosslinking trend at higher doses due to the termination reaction of the fragments of degraded molecules and due to intramolecular radical termination, decreasing the rate parameter.

The values of the Avrami slope parameter (n) as a function of the irradiation dose for the samples irradiated in acetylene appeared to be slightly higher although the overall results didn't show any meaningful differences. Samples were stabilized and irradiated also in acetylene to doses as high as 160 kGy (data not shown) and they showed a smaller tendency of decreasing for the rate parameter with dose increase. This was consistent with a smaller crosslinking yield due to the content of stabilizer. The overall data showed that the process of crystallization was slowed down by higher irradiation doses due to the increase in crosslink density. However, from the comparison of the rate parameter taken at 1 and 55% crystallization, one could suppose that there was an initial nucleating effect with its kinetics slowed down by the entanglements originated by the high level of crosslinking and/or grafting. Apparently, this point is exactly below the gelling dose, i.e., after moderated degradation and formation of microgels, but before their connection in a network restricting the nucleation.

Table 3 showed only the results of PP irradiation in reducing and crosslinking atmosphere considering that effects of PP irradiation in air and N_2 are well-known (Yoshi et al., 1986b,c). Samples 2–4 in Table 3 showed the results from electron irradiation of PP in a crosslinking atmosphere. From the SEC results of Mn, Mw and Mz, the main chain scission can be easily

observed, even at doses as low as 3 kGy. However, from 3 to 15 kGy, one can verify an increase in M_z , stabilization of M_w and decrease in M_n . Clearly, only degradation was occurring at the earliest stages of irradiation and the mechanism changed with dose, favoring crosslinking of lower molecular weight molecules, probably due to double bond formation and grafting on the PP main chain. Samples 5–8 showed a smaller decrease of M_n , gamma irradiated in reducing/crosslinking atmosphere, and even an increase in M_w and M_z . The results from DSC in Table 3 showed a pronounced nucleating effect. The crystallization temperature increased from 387 to a limit of about 393 K. This was explained by the formation of microgels, i.e., highly branched molecules. In connection with the SEC data, it was realized that the very high molecular weight fraction of the polymer changed from linear molecules to branched ones.

4. Conclusion

The results showed that degradation was the major reaction in the initial step of irradiation irrespective of the atmosphere and/or antioxidant. However, double bond formation increased the production of branching and crosslinking reactions. A PP was obtained with very high melt strength at low dose, indicating that the control of the branching reaction was useful for the production of a polymer with special rheological properties.

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