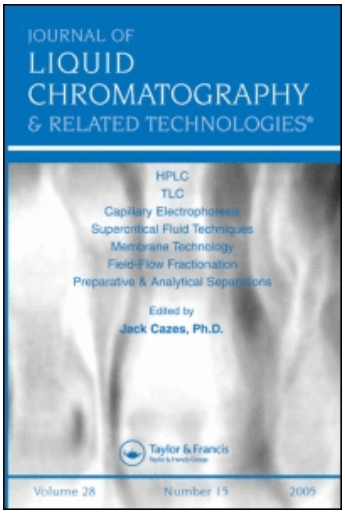

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MWD OF i-POLYPROPYLENE UNDER DEGRADATION BY SELC USING A NEW ELUTING SOLVENT

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ABSTRACT

A new eluting solvent, cyclohexane, for steric exclusion liquid chromatography (SELC) at 70°C of i-polypropylene (PP) has been applied to the study of molecular weight distribution (MWD) of samples of PP under repeated extrusion and under oxidative degradation in the presence of incorporated organic peroxide. Various parameters characterizing the changes in MW and MWD of the samples are listed in TABLE 1. M_z changed pronouncedly with increasing extent of degradation in both degradation processes, while M_n changed very slightly indicating the average number of chain scission per chain had been very small, much less than one. Difference in the mechanism of the mechanical as compared to the oxidative degradation has shown up in the way the low MW end of the MWD curves changed during the progress of the degradation process.

INTRODUCTION

Since the discovery of isotactic polypropylene (PP) by Natta and his coworkers, PP has been widely used as plastics, films and

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fibers of diversified end uses. Some difficulties of processing had been experienced originated from the high molecular weight (MW) tail of the extremely wide molecular weight distribution (MWD) of PP resin produced commercially. Fan et al. (1) found that the high MW tail in the MWD of PP resin is of key importance to the structure development on the spin line in the melt spinning process while the low MW end in the MWD might affect the strength of the fiber obtained. Controlled degradation of PP has been an important means of MW and MWD adjustments of the resin to achieve easy processing and high quality products in injection molding and in the manufacture of fibers. Consequently characterization of MWD of PP during processing and degradation is of paramount importance. For the determination of MWD of polymers steric exclusion liquid chromatography (SELC) is the most useful method. However, SELC for PP has to be conducted at high temperature, say 135–145°C, using toxic halogenated aromatic compounds as eluent. In the present paper a new eluting solvent for SELC of PP (2) at 70°C has been applied to the study of changes in MWD of two series of PP samples, one under repeated extrusion degradation and the other under oxidative degradation.

EXPERIMENTAL

Samples

Two commercial PP resins were used in this investigation. The resin S1 containing usual additives was subjected to repeated extrusion for m times at 250°C to give a series of samples S1(m). The resin S2 was incorporated with n parts of an organic peroxide per 10,000 parts of the resin and pelletized by extrusion at 200°C to give a series of samples S2(n). The resin S1 was produced by Xiang Yang Chemical Co., Beijing and the resin S2 was produced by Lanzhou Chemical Co., Lanzhou.

SELC

PP samples were first dissolved in small amount of decalin at 140°C for two hrs and then diluted with hot cyclohexane at 70°C, and the solution was kept at 70°C. The content of decalin in the solution was kept less than 8% wt. The solution was filtered through 0.5 μm filter before entering the SELC column. SELC was run on Waters ALC/GPC Model 150C with two linear Shodex KF-80M columns in series operated at 70°C with cyclohexane as the eluent at a flow rate of 1 ml/min (2). The column was calibrated with a series of narrow MWD standard polystyrene samples from Waters Associates and i-PP fractions furnished by National Physical Laboratory (NPL), United Kingdom. Linear calibration relations were obtained as shown in Figure 1. The SELC peak MW values given by NPL for the PP fractions were used for all MW evaluations.

RESULTS AND DISCUSSION

The reliability of MWD obtained by SELC in the present investigation was checked by the mixed sample method. The integral MWD curves of two PP samples, one was a commercial resin S3 of M_w $3.4 \cdot 10^5$ from Xiang Yang Chemical Co. and the other was one of the BPL fraction F1 of M_w $1.5 \cdot 10^5$, were determined separately. Then the integral MWD curve for a mixture of 79.5% wt F1 and 20.5% wt S3 was determined and compared to a calculated curve from additivity of the integral MWDs of F1 and S3. Satisfactory agreement of the experimental data with the calculated curve from additivity was observed as shown in Figure 2.

Both series of degraded PP samples S1(m) and S2(n) showed narrowing of the MWD with increasing degree of degradation. Pronounced cut in the high MW tail of the MWD should be noted as shown in Figures 3 and 4. The MWD of a polymer is usually characterized by the ratio M_w/M_n. In this laboratory it has been found that M(90)/M(50) and M(50)/M(10), where M(10), M(50) and M(90)

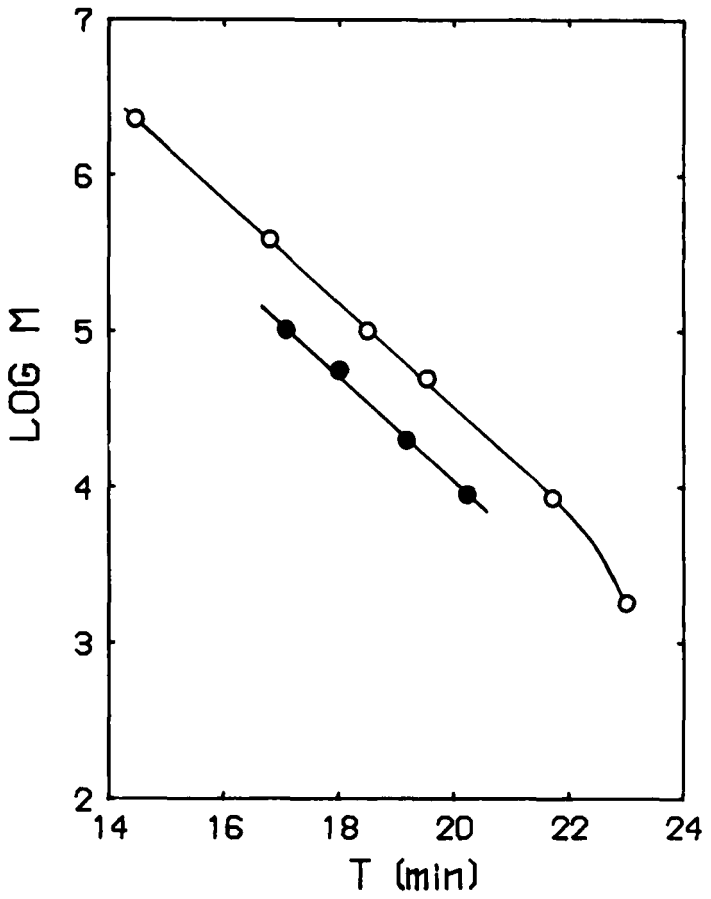

FIGURE 1. SELC calibration curves for the Shodex KF-80M column. Open circles, narrow MWD standard PS samples; Filled circles, BPL PP fractions.

are MW values at 10, 50 and 90% respectively of the integral MWD curve I(M), are even more useful for MWD characterization (3,4) to show the effects of high and low MW tails in the MWD on the mechanical properties of the sample. Parameters characterizing the MW and MWD of PP samples of this investigation are listed in Table 1. It should be mentioned here that all MW values listed

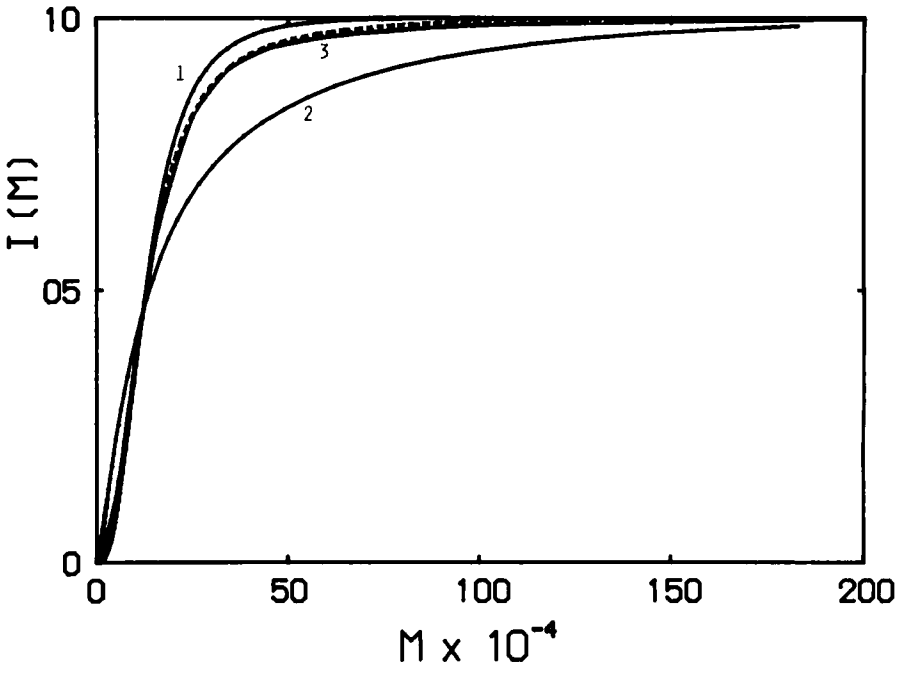

FIGURE 2. Integral MWD curves of 1-PP fraction F1, 2-sample S3, brocken curve-mixed sample of 79.5% wt F1 + 20.5% wt S3, 3-calculated curve from additivity of curves 1 and 2.

TABLE 1 Parameters Characterizing MW and MWD of the PP Samples

$MW \cdot 10^{-4}$

Sample	M_n	M_w	M_z	M_z/M_w	M_w/M_n	M(10)	M(50)	M(90)	$\frac{M(90)}{M(50)}$	$\frac{M(50)}{M(10)}$
S1(2)	3.93	26.8	94	3.5	6.8	1.84	12.9	77	6.0	7.0
S1(4)	3.39	24.4	83	3.4	7.2	1.59	11.8	70	5.9	7.4
S1(8)	3.56	21.9	69	3.2	6.2	1.76	11.5	62	5.4	6.5
S2(0)	3.15	21.2	59	2.8	6.7	1.64	12.7	58	4.6	7.7
S2(1)	2.58	16.8	44	2.6	6.5	1.35	10.8	45	4.2	8.0
S2(2)	2.71	16.2	48	2.5	6.0	1.53	11.1	42	3.8	7.3
S2(3)	2.41	11.9	27	2.3	4.9	1.48	8.5	30	3.5	5.7

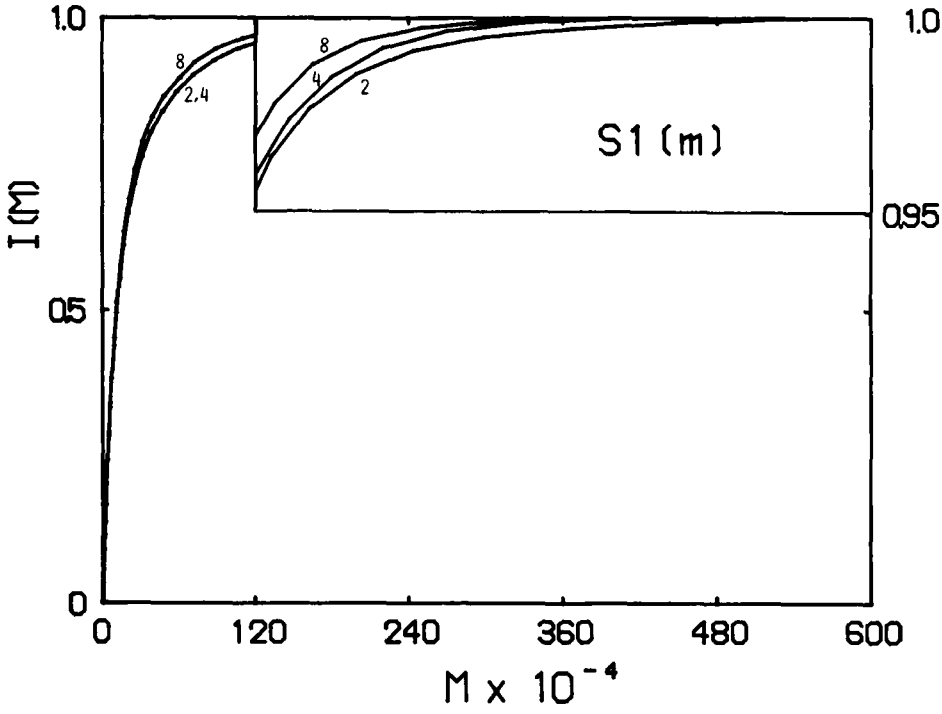

FIGURE 3. Integral MWD curves of the samples S1(m). Numbers refer to the value of m.

are based on the SELC peak MW given by BPL fractions. We take all the evaluated MW values for granted in this paper although they appear to us much too high as compared to intrinsic viscosities determined in decalin at 135°C (5) and zero shear rate melt viscosities determined by falling sphere method at 230°C (6) on some of these samples.

Decrease of average MWs M_n, M_w and M_z with increasing extent of degradation is shown in Figures 5 and 6. Obviously M_z is much more sensitive to the extent of degradation than M_w. Similar behavior have been mentioned by Cazes in the thermal degradation of PP in solution (7). M_n decreased very slowly with increasing

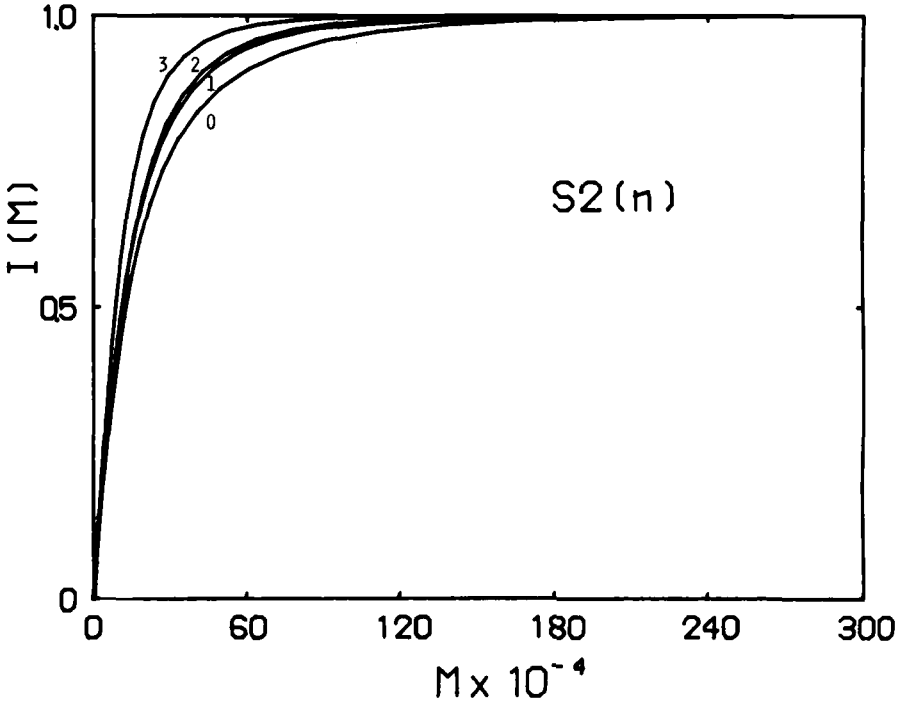

FIGURE 4. Integral MWD curves of the samples S2(n). Numbers refer to the value of n.

n in the oxidative degradation process and appeared almost unchanged with m up to eight times of extrusion. As every chain scission will lead to an increase of the number of chains by one it is easily seen that

$$\frac{M_n(0)}{M_n(s)} - 1 = \frac{s}{N}$$

where s is the number of chain scissions among N chains present. For the case of the PP sample S2(3) only 30% of the chains had undergone a chain scission, yet drastic changes occurred in M_z and MWD.

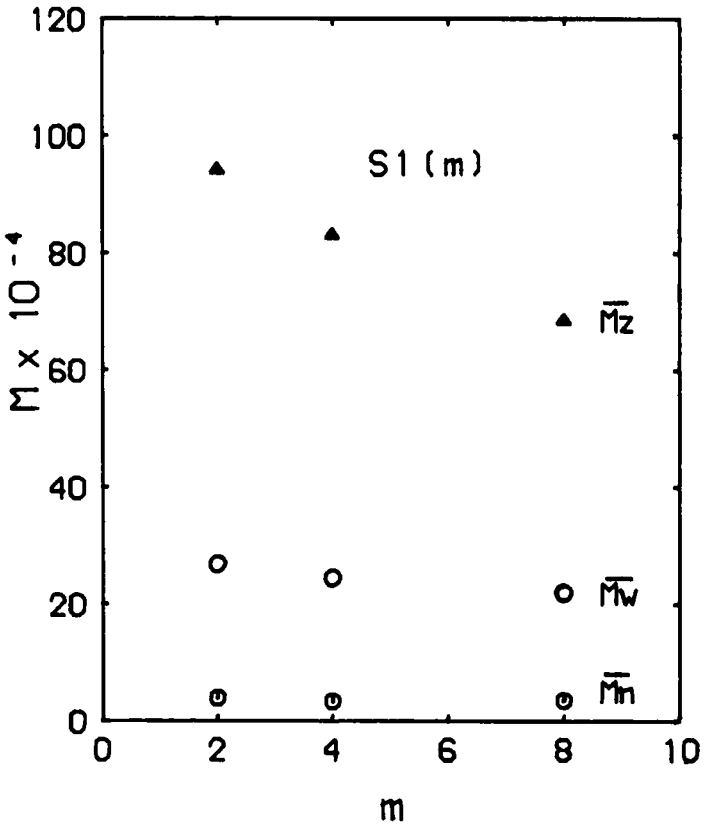

FIGURE 5. Changes in average MWs with the number of repeated extrusion m.

As the value of M_z of a sample depends very much on the precision of the high MW end and that of M_n of the low MW end of the MWD of the sample, being both difficult experimentally, we believe the use of M(90)/M(50) and M(50)/M(10) will be more practical and easy than the ratios M_z/M_w and M_w/M_n to characterize the high and low MW ends of the MWD. Data in Table 1 demonstrate clearly the usefulness of M(90)/M(50) and M(50)/M(10) to characterize the degradation processes.

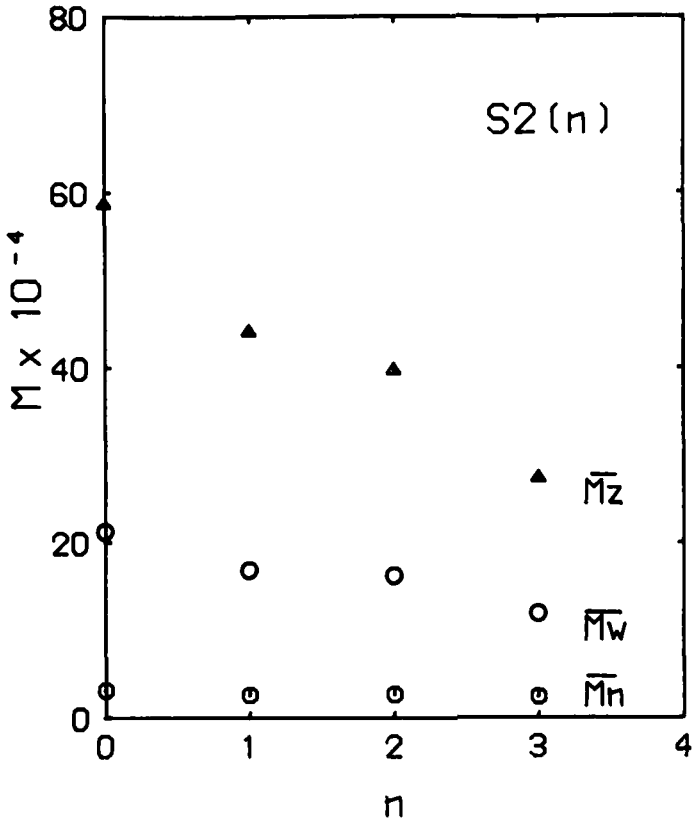

FIGURE 6. Changes in average MWs with increasing amounts of an organic peroxide incorporated into S2 during pelletizing. n is parts peroxide per 10,000 parts PP resin.

It is known that mechanical degradation has a lower bound in MW below which the chain scission will not be possible (8,9) while oxidation degradation might involve a completely random scission of the chain, some difference in the low MW end of the MWD with increasing extent of degradation should be expected. In the case of mechanical degradation M(50) and M(10) should approach certain value as degradation proceeds, while in the case of oxidative de-

gradation they should decrease steadily with increasing extent of degradation. This seems to be borne out by the experimental results as shown in Figures 3 and 4 and Table 1.

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