The Study of p-Tert-Butylcalix[n]arene on γ-Radiation Stabilization of Polypropylene

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ABSTRACT The γ-radiation effect of polypropylene was investigated in the presence of three kinds of p-tert-butylcalix[n]arene(n=4,6,8) in air or in vacuum at ambient temperature. The influence of radiation dose and store time upon the mechanical properties of the irradiated PP sheets were measured.The results showed that the radiation stabilization was reduced with the increase of the ring size of calixarenes. Based on the mass spectra and the analysis of post-irradiated product,the mechanism of radiation degradation of p-tert-butylcalix[4]arene has been proposed.

KEYWORDS Calixarene, Polypropylene, γ-Radiation, Mechanical properties

INTRODUCTION

Although the phenolic cyclic oligomers -----calixarenes were claimed to be separated from the reaction between phenol and formaldehyde in the 1940s they did not bring attention until 1980s due to the pioneering work by C.D. Gutsch[1]. Because of their easy availability, convenient modification on both upper and lower rims as well as the intriguing functions such as the high selective complexiation towards metal ions and high stability they are considered as "probably the only class of macrocyclic host molecules which combine easy accessibility with a large variety of structures" and become widely applied in polymer field [2]. Calixarenes and their derivertives were found to be good antioxidants, thermal and phto stabilizers, key modified component for the thermosetting resins and antiagers for plastics[3-8].

Seiffarth reported that calixarenes were effective light and heat stabilizers for polyolefins[8]. The unmodified calix[n]arenes (n=4, 6, 8) showed almost the same effect in UV-resistance as hydroxyl-substituted bezophenone. Ninagawa conducted the photochemical experiment with poly(vinyl chloride) membrane to demonstrate the higher UV-resistant performance with cyclic type calixarenes than their non-cyclic type ones[9]. The γ-radiation stability of polypropylene (PP) was found to be improved in the presence of p-tert-butylcalix[4]arene especially at higher dose compared with the case of BHT[10]. Polypropylene is one of the most frequently used polymers in the manufacture of medical disposables. Its degradation on g-radiation and post-irradiation can be minimized by introducing suitable hindered phenols[11]. The structural specialities and the already-displayed applications as antioxidants may render calixarenes become a new type of stabilizers against oxidative degradation of polypropylene under irradiation.

In the present paper three calix[n]arene (n=4, 6, 8) with different ring size are empolyed to investigate the g-radiation effect of polypropylene containing these components in air or in vacuum at ambient temperature.

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EXPERIMENTAL

1.Material

P-tert-butylcalix[n]arene (CA[n], n=4, 6, 8) were synthesized according to the literatures in yield of 43%, 60% and 80%[12-14]. Their structures were confirmed by MS, IR, ^{1}H NMR and elemental analysis. 2,6-Di-tert-butyl-p-cresol (BHT) was obtained from Shanghai Chemical Reagents Station. Isotactic PP powder containing no commercial additives was supplied by Yanshan Petroleum and Chemical Company.

2. Preparation of Samples

The stabilizers (0.3 % w/w) were solvent blended into the polymer powders using toluene followed by evaporation of the solvents and then by extrusion into lines. The cut lines were compression moulded into dumbbell-shaped sheets by moulding chips under a pressure of 150 kg.cm^{-2} for 20 min (compression time) and 15 s (injection time) at 190℃. The sheets were then immediately cooled between the two plates of a cold press at room temperature. The thickness of the sheets is 2.0 mm.

3. Irradiation

The samples were irradiated in air or in vacuum with Co-60 gamma rays at a dose rate of 6.5 kGy h^{-1}. P-tert-butyllcalix[4]arene was irradiated with electron beems at a dose rate of 4.0 X10^3 kGy h^{-1}. To keep the heat history the unstabilized PP was also processed at the same condition.

4. Measurement of Mechanical Properties

Tensile strength at break and elongation at break were determined from stress-strain curves. The tension speed used was 50 mm min^{-1}using WD-5 Electron Universal Testing Equipment. The variation of the change of radical concentration was measured by electron spin resonance(BRUKER ESR ER 200 DSRC).

RESULTS AND DISCUSSION

1. Mechanical Properties

Fig.1~Fig.4 show the variations of tensile strength at break and elongation at break of irradiated CA[n]-PP (n=4, 6, 8) and BHT-PP with dose in air or in vacuum. It has been reported that PP degrades during irradiation because of chain scission with the decrease in the molecular weight of PP[15]. The decrease in the tensile strength and elongation at break reflect the degradation of PP. From Fig.1 and Fig.2, on comparing BHT-PP,CA[4]-PP,CA[6]-PP and CA[8]-PP, it can be clearly seen that the overall tendency in tensile strength at break is in the order of CA[4]-PP > CA[6]-PP~ BHT-PP > CA[8]-PP. It is noteworthy for CA[4]-PP that after a rapid decrease at around 25 kGy, the tensile strength at break takes a much slower fall. The strength is almost maintained within the dose range from 40 to 120 kGy. In contrast, no data was obtained for BHT-PP, CA[6]-PP and CA[8]-PP after 100 kGy due to breaking of the testing sheet. In vacuum as shown in Fig.2 CA[4]-PP follows a similar trend, i.e., it gives a very slow decrease in tensile strength compared to BHT-PP and other two PP sheets containing calix[n]arene (n=6, 8).

Among the three calixarenes in both cases (air and vacuum) as shown in Fig.3 and Fig.4 the elongation at break for CA[4]-PP is larger than the other two. The higher tensile strength at break observed in vacuum than in air may be due to more efficient crosslinking in vacuum[16]. The lower elongation of CA[6]-PP and CA[8]-PP than that of CA[4]-PP may indicate that the

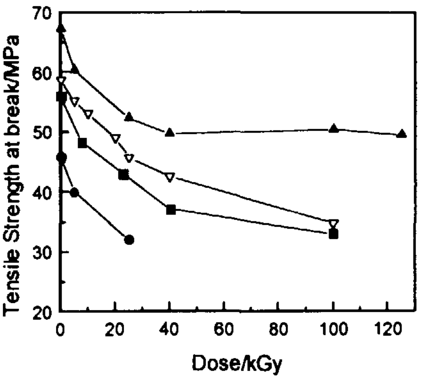


Fig.1 Tensile strength at break at different doses in air
CA[4]-PP(▲);CA[6]-PP(■);
CA[8]-PP(●); BHT-PP(▽);

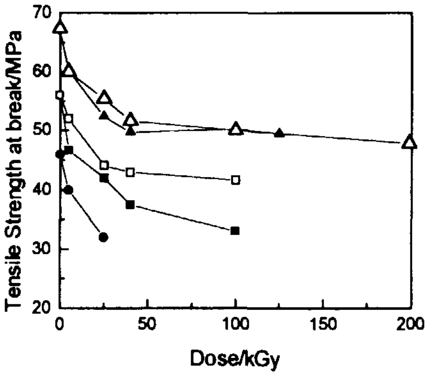


Fig.2. Tensile strength at break at different doses
In air: CA[4]-PP(▲);CA[6]-PP(■); CA[8]-PP(●);
In vacuum:CA[4]-PP(△);CA[6]-PP(□);

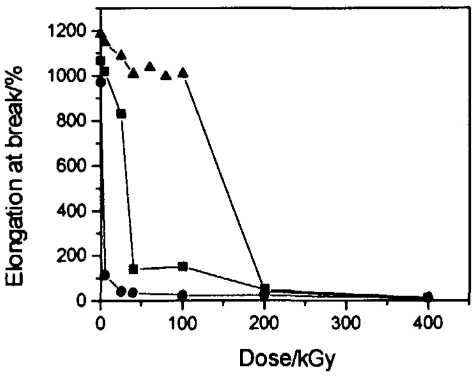


Fig.3. Per cent elongationat break at different doses in air
CA[4]-PP(▲);CA[6]-PP(■); CA[8]-PP(●);

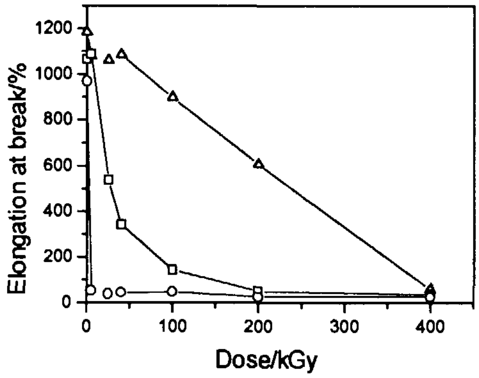
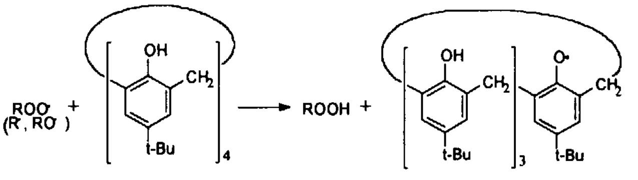


Fig.4 Per cent elongation at break at different doses in vacuum
CA[4]-PP(△);CA[6]-PP(□);CA[8]-PP(O);

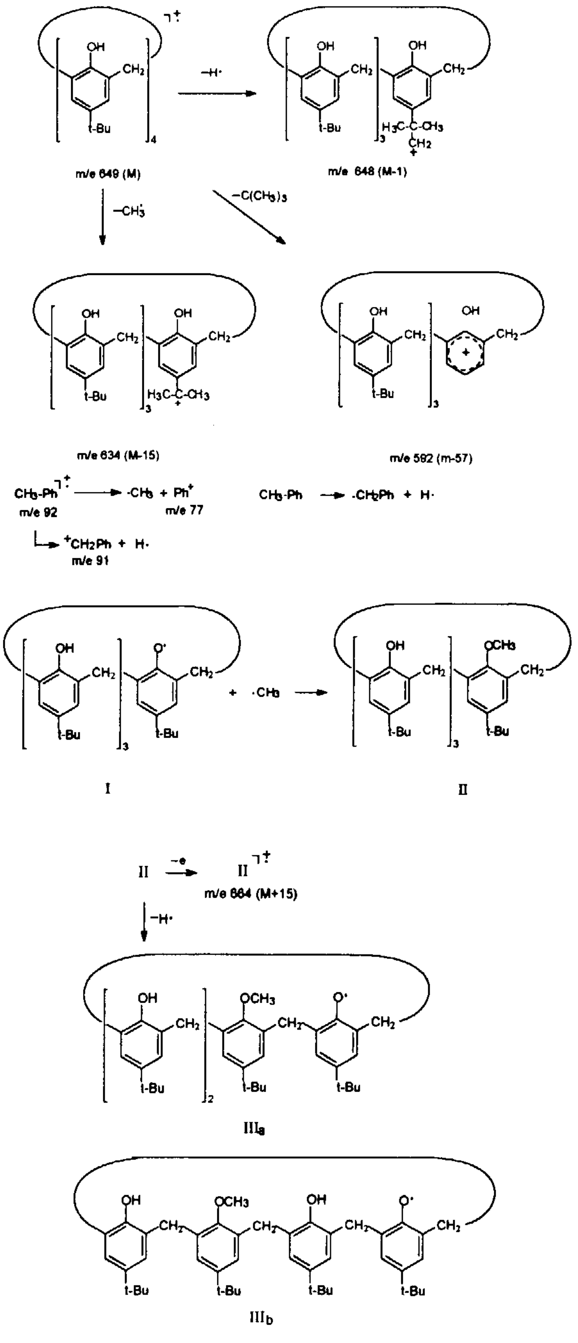
presence of p-tert-butylcalix[4]arene suppresses the degradation more effective especially at higher dose (40~100 kGy). The possible stabilization mechanism is that the calix[4]arene reacts with peroxy radical of PP chain and turned to a stable radical (I) which was stable enough and could not react further with PP chain.

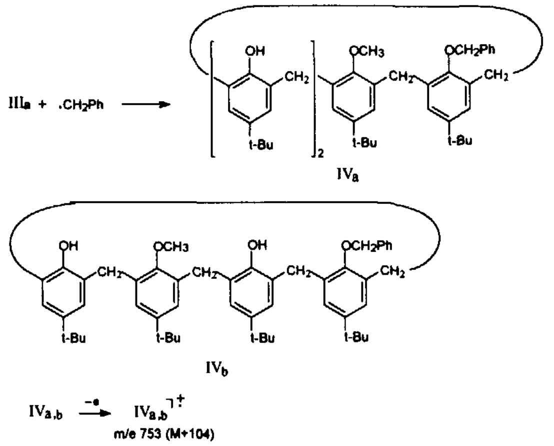


From the ESR spectra of γ-irradiated p-tert-butylcalix[4]arene, the signal remained with higher intensity for a long time. This indicates the presence of stable phenolic radicals resulting from calix[4]arene.

Within the dose range (< 1000 kGy) applied, no change of calix[4]arene backbone was observed by IR, MS and ^{1}HNMR spectra before and after irradiation. This shows the structure of p-tert-butylcalix[4]arene can keep stable at dose at least up to 1000 kGy. The hindered phenols, including BHT, are prone to be structurally changed into quinones[17]; but p-tert-butylcalix[4]arene is more resistant to irradiation. At higher dose rate (4.0×10^{3} kGy/h) and dose the calix[4]arene begins to be destructed with the change of IR spectra. Thus the stability of p-tert-butylcalix[4]arene may partly account for the radiation stabilization of polypropylene especially at higher doses.

The calix[4]arene is subjected to analysis of mass spectra before and after irradition. At lower dose rate (6.5 kGy/h) the maximum peak indicated only presence of molecular ion m/e 649; whereas M+104 was observed at 4.0 × 10^3 kGy/h and 2.0 × 10^4 kGy. The separation from the irradiated sample provides compound II, whose structure is in line with the reported literature[18]. Based on the observation the mechanism is proposed as follows:





2.Storage Time

To test the storage stability of polypropylene containing calixarene after irradiation in air, the variations of tensile strength at break and elongation at break were traced within four months as shown in Fig. 5 and Fig.6.

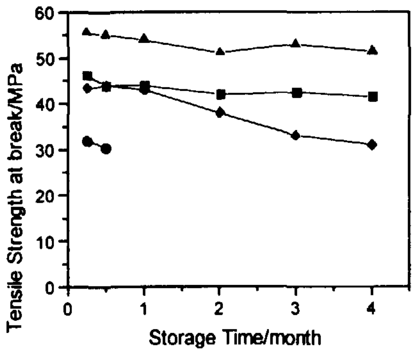


Fig.5 Variation of tensile strength with storage time in air, 25 kGy CA[4]-PP(▲); CA[6]-PP(■,); CA[8]-PP(●); BHT-PP(◆);

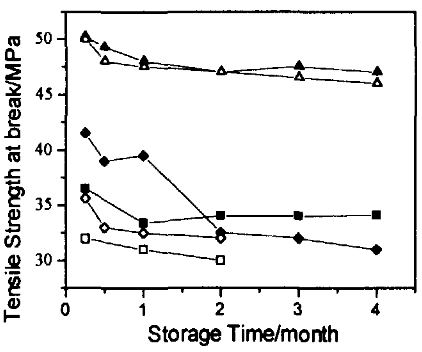


Fig.6 Variation of tensile strength with storage time in air, 40 kGy ;100 kGy; CA[4]-PP(▲,△);CA[6]-PP(■,□); BHT-PP(◆,◇);

At 25 kGy the tensile strength gives no obvious change within the first month except for CA[8]-PP and then almost remains constant. BHT-PP keeps a continuous decrease in the latter hree months while CA[4]-PP and CA[6]-PP kept unchanged. The similar tendency was observed at the dose of 40 kGy. As the dose is raised to 100 kGy, the difference grows wide among the three samples. CA[4]-PP gives nearly the same result at 40 and 100 kGy, but the specimen of BHT-PP and CA[6]-PP fall at 40 kGy and at 100 kGy ,they became brittle two months later and no comparing data were obtained.

Thus CA[4]-PP stands out among the samples investigated at two different doses. At higher dose the effect brought by the presence of calix[4]arene becomes more obvious. At lower dose (25 kGy) calix[6]arene shows better degradation-resistant than BHT in the latter stage after irradition.

3. Thermal Properties

The thermal stability of the irradiated samples with different stabilizers can be understood by TG analysis. Generally, decomposition temperature decreases gradually with dose due to the chain scission induced by radicals. The sample containing CA[4] gives a relatively higher decomposition temperature. For instance, at dose of 25 kGy, CA[4]-PP decomposed at 327℃ compared to 306℃ for PP and 320℃ for BHT-PP respectively. This may indicate that CA[4] in the polymer functions better to suppress scissions caused by the irradiation than BHT.

In the DTA experiment there was little difference in melting points among PP with and without additives in air. In all cases , melting points decreased with irradiation dose. The trend is in accord with the documented results[19]. However, with dose of around 40 kGy CA[4]-PP began to melt at temperature 4~8 ℃ higher than PP; no change was observed in BHT-PP and CA[8]-PP, suggesting better stabilizing effect in CA[4]-PP.

CONCLUSIONS

1. The g-radiation stabilization effect on polypropylene was increased in the order of CA[4]-PP > CA[6]-PP~ BHT-PP > CA[8]-PP in air or in vacuum at ambient temperature. The additive effect of the calix[4]arene is almost maintained in the dose range of 40~100 kGy; however, that of BHT is not so evident in the same dose range.
2. PP is stabilized more efficiently in the presence of the calix[4]arene at higher dose than with BHT, calix[6]arene and calix[8]arene. The stability of p-tert-butylcalix[4]arene against irradiation up to at least 1000 kGy was observed. The better inhibiting effects at higher dose seem to be attributable to the durability of the calix[4]arene skeleton.

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