Synthesis and Characterization of a Novel Nitrogen-Containing Flame Retardant

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ABSTRACT: The lowering of ignitability and flammability of polyethylene (PE) and the production of fire-retarding materials has become an urgent problem because of the demand of fire safety. In our article, a new charring agent (CA), a derivative of triazines, was synthesized by charging 2-amino-4,6-dichloro-s-triazines and diethylenetriamine into a reactor to conduct the solution polycondensation reaction, and the synthetic conditions of monomer and CA, such as temperature, time, etc., were investigated. Both the monomer and the resulting polymer were characterized by mass spectrum (MS), Fourier transform infrared (FTIR) spectroscopy, ^{1}H-NMR, and elemental analysis. The intrinsic viscosities and flame-retardancy property of CA were also studied. It was found that the incorporation of ammonium polyphosphate (APP) and CA into low-density polyethylene (LDPE) has a distinct effect on thermal and flame-retardancy behavior. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1556–1561, 2004

Key words: charring agent; flame retardance; synthesis; characterization; polyethylene

INTRODUCTION

It is known that the halogenated compounds were good fire-retardant additives for polyethylene (PE), especially in synergistic combination with antimony trioxide, but there are serious disadvantages about the evolution of toxic gases and corrosive smoke. It was recently reported that some currently used brominated aromatic fire retardants may form highly toxic brominated dibenzodioxines and dibenzofurans while burning.[1,2] In the search for halogen-free flame retardants, intumescent flame retardants (IFR) have recently received considerable attention, and especially in the flame retardation of polyolefin, they manifested good efficiency.[3–5]

IFR systems, first used in the painting industry, were applied to the fire stabilization of polymeric materials in the last 30 years. The action of IFR is mainly through a condensed-phase mechanism. While burning, it gives a swollen multicellular char. The typical formulation of IFR is made of three constituents: an essentially phosphorus-containing additive, whose purpose is to form, during the combustion, an impermeable, semisolid, and vitreous layer essentially composed of polyphosphoric acid and to activate the process of formation of intumescence; a second additive, containing nitrogen, which serves as foaming agent; and a third, carbon-containing additive, which acts as a carbon donor to allow an insulating cellular carbonaceous layer (char) to be formed between the polymer and flame.[6–9] This kind of flame-retardant system is environmental-friendly and offers numerous advantages (i.e., absence of corrosion phenomena in machinery in which the polymers are processed, a lower emission of smoke as compared to systems containing halogenated hydrocarbons and metal compounds, and, above all, the possibility of endowing the polymer with satisfactory flame-proof properties with a smaller total additive amount and therefore without excessively impairing the mechanical properties thereof).

Recently, it was found that triazine and its derivatives are good charring agents because of its abundant nitrogen and structure of tertiary nitrogen.[10] Owing to the synergism between element N and P, it shows excellent charring effect associated with ammonium polyphosphate (APP).

In this article, we mainly aim to design and synthesize a new flame retardant containing N, which is a charring agent, CA (Scheme 1), and to investigate the synthesis of monomer and polycondensation conditions, such as temperature, time, etc. The structure of monomer and resulting polymer is characterized by
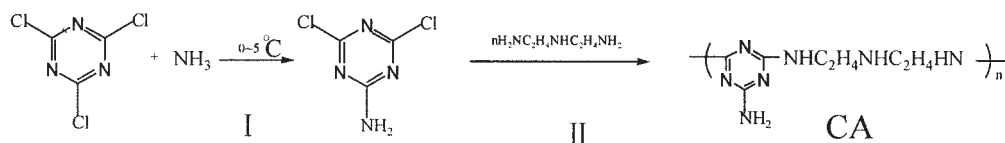
Scheme 1 The synthetic route of CA.

mass spectra (MS), Fourier transform infrared (FTIR) spectroscopy, ^{1}H-NMR, and elemental analysis. The flame retardancy and intrinsic viscosities are also characterized.

EXPERIMENTAL

Materials

Cyanuric acid chloride was purchased from Wuqiao Chemical Factory (Hebei, China) and was purified via its recrystallization from acetone. Diethylenetriamine, ammonia, sodium carbonate, sodium bicarbonate, and acetone were provided by Changzheng Chemical Reagent Corp. (Shanghai, China). APP was supplied by Chengdu Academy of Chemical Engineering and Design (Chengdu, China). Commercial low-density polyethylene (LDPE; 1I2A) was provided by Yangzi Petroleum Chemical Company (Nanjing, China).

Preparation of 2-amino-4,6-dichloro-s-triazines[11,12]

In a 1000-mL glass flask, equipped with stirrer, thermometer, and cooling bath, a fine slurry of cyanuric acid chloride was prepared by running a thin stream of a hot solution of 92 g (0.5 mol) cyanuric acid chloride in 250 mL of hot acetone into 300 mL of well-stirred ice-water. Then, 10.2 g (0.6 mol) of ammonia and 42 g (0.5 mol) of sodium bicarbonate were added while maintaining the temperature at 0–5°C, and the mixture was stirred for about 1 h, until the carbon dioxide release is completed. Successively, 300 mL ice-water was added, and the product was filtered and washed free of chloride ion with cold water. The product was dried to a constant weight *in vacuo* at 50°C. The weight of product was 70 g; the conversion was 84.1% and the melting point of the purified product was ∼ 233–236°C.

Preparation of N-containing CA

In a 1000-mL glass flask, equipped with stirrer, thermometer, feeding funnel, condenser, and heating bath, 50 g (0.30 mol) 2-amino-4,6-dichloro-s-triazines and 200 mL H_2O were added; then, the mixture was stirred at 50°C while 35 g (0.34 mol) diethylenetriamine and a solution consisting of 32 g (0.30 mol) sodium carbonate in 100 mL of water were fed within 30 min to keep the reaction system neutral. Thereafter,

the mixture was heated to 100°C and kept under reflux for about 2 h. Then, the whole mixture was cooled to room temperature, and the product formed was filtered and washed through the filter with water. The product was dried to a constant weight *in vacuo* at 80°C, and the weight of product was 51 g.

Preparation of flame-retardant PE samples

The total content of CA and APP in PE was always kept at 30 wt %, and PE samples of various APP/CA formulations were prepared by using a counter-rotation twin-screw extruder under the following standard conditions: average residence time, 25 s; rotation of screw, 80 prad/min; mixing temperature, 150°C.

After mixing, the samples were hot-pressed under 10 MPa for 5 min at 150°C into sheets of suitable thickness and size according to the corresponding test standard.

Characterization

The structure of monomer was determined by MS measurement, which was performed on a Finnigan-4570 mass spectrum analyzer. The ^{1}H-NMR of monomer was conducted with a FT-80A NMR by using DMSO as a solvent and TMS as an internal standard. The ^{1}H-NMR of CA was conducted with a FT-80A NMR by using CF_3COOH as a solvent and TMS as an internal standard. The intrinsic viscosities of CA were determined by an Ubbelohde viscometer at 25 ± 0.1°C in the DMF solution. FTIR spectra were recorded with KBr powder by using a Nicolet FTIR 170SX infrared spectrophotometer. The elemental analysis was determined by Carlo Erba-1106 elements analyzer. Melting point was measured with a XRC-1 melting point analyzer. Limited Oxygen Index (LOI) values were measured on a JF-3 oxygen index meter (Jiangning, China) with sheets measuring 130 × 6.5 × 3 mm according to ISO4589-1984.

RESULTS AND DISCUSSION

The first Cl atom on cyanuric acid chloride has higher activity, but the second Cl atom has lower activity owing to the passivation effect of substituent (—NH_2). Therefore, the replacement reaction between ammonia and cyanuric acid chloride has extremely high selec-
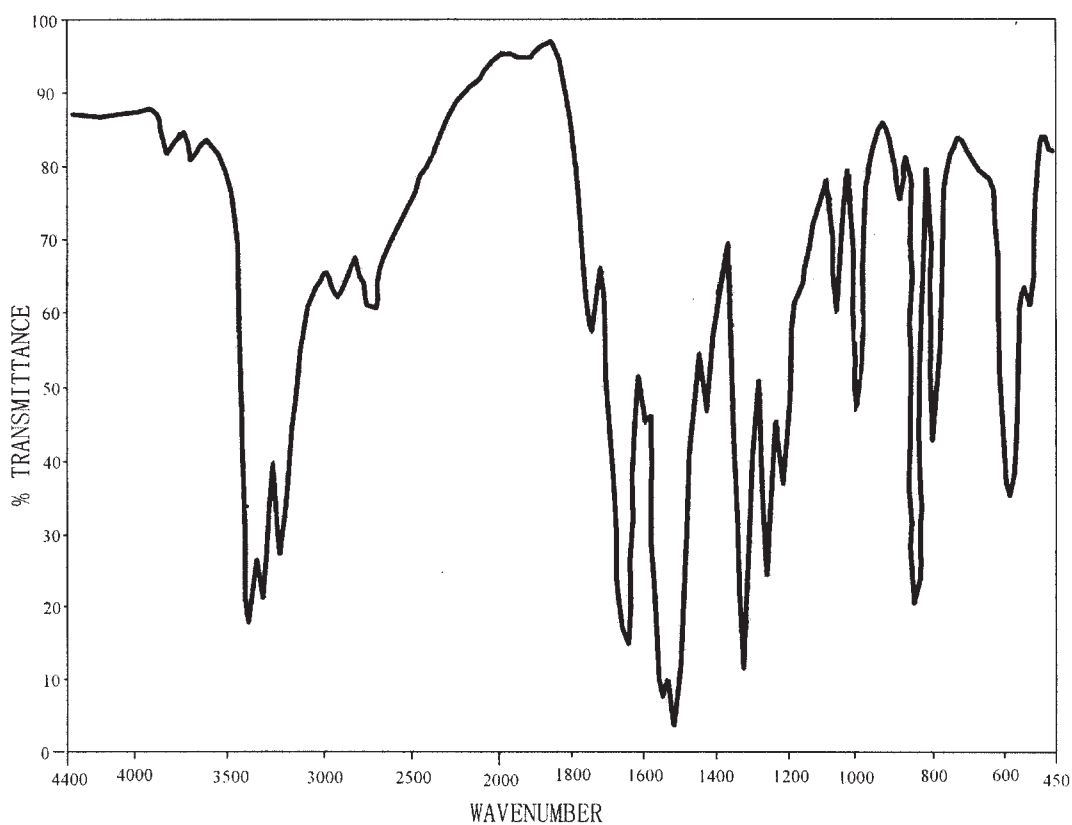
TABLE I
The Influence of Reaction Temperature on Intrinsic Viscosity of Production CA

Dripping stage (°C)	Polymerization stage (°C)	Color of CA	η_{int} (dL/g)
None	100	Deep yellow	0.09
70	100	Yellow	0.13
60	100	Yellow	0.15
50	100	Slightly yellow	0.18
40	100	Slightly yellow	0.17

TABLE II
The MS Data and Its Corresponding Fragment of Monomer

Fragment peak	Fragment
164	M^+
129	
87	
68	

tivity for temperature, and no side reactions will appear because of superfluous ammonia. Hence, we can make the reaction fully completed by the addition of superfluous ammonia.

The mechanism of polycondensation is akin to that of condensation in the synthesis of small molecules. Reactions (I) and (II) could be considered as a S_{N2} Lewis acid–base reaction, and it can be described as

As described above, the second and third Cl atoms can only be substituted at >40 and 100°C, respectively. Therefore, we adopted the solution polycondensation to avoid the production of the overfull by-products in melt polycondensation because of higher reaction temperature. According to the classical polycondensation theory, the degree of polymerization X_n = $\sqrt{(K/P_{nw})}$ and the equation $(d \ln K)/dT = (\Delta H/RT^2)$ indicate that equilibrium constant K is correlative to the enthalpy variety, ΔH. Therefore, the molecular weight is dependent on the equilibrium constant K and reaction temperature T, so the pH value was kept at 7–8 by continuously adding sodium carbonate to eliminate the produced H^+ to increase the molecular weight. We have investigated the effect of reaction

temperature on the intrinsic viscosity of CA (Table I) by adopting the dripping manner for diethylenetriamine and two-stage reaction: the reaction time of the first dripping stage was kept to 30 min, and the polymerization time of the second stage was kept to 2 h.

Figure 1 shows the MS spectrum of the monomer 2-amino-4,6-dichloro-s-triazines. The main fragment peak and its corresponding fragment are listed in Table II. The FTIR spectrum of monomer is shown in Figure 2. Absorptions of v_{N-H} at 3318 cm^{-1}, v_{tr-Cl} at 1014 and 536 cm^{-1}, respectively, indicate the replacement of amido (—NH$_2$). Figure 3 shows the ^{1}H-NMR spectra of monomer. The broad resonance corresponding to —NH$_2$ was observed at 8.77 ppm, and this chemical shift moved downfield because of the absorbing electronic effect of Cl atoms and resonance effect of the triazines ring. The weak and broad peak at about 11.80 ppm, which was an impure peak, should be assigned to the active —OH produced by hydrolyzation of —Cl on the triazines ring. The multiplet between 2.48 and 2.52 ppm corresponded to the solvent DMSO protons. All these facts allowed us to conclude that the sole replacement of cyanuric acid chloride was successful.

Figure 4 shows the FTIR spectrum of CA. Absorptions of $v_{-C-N-C-}$ from diethylenetriamine were ob-

Figure 1 The MS spectrum of monomer.

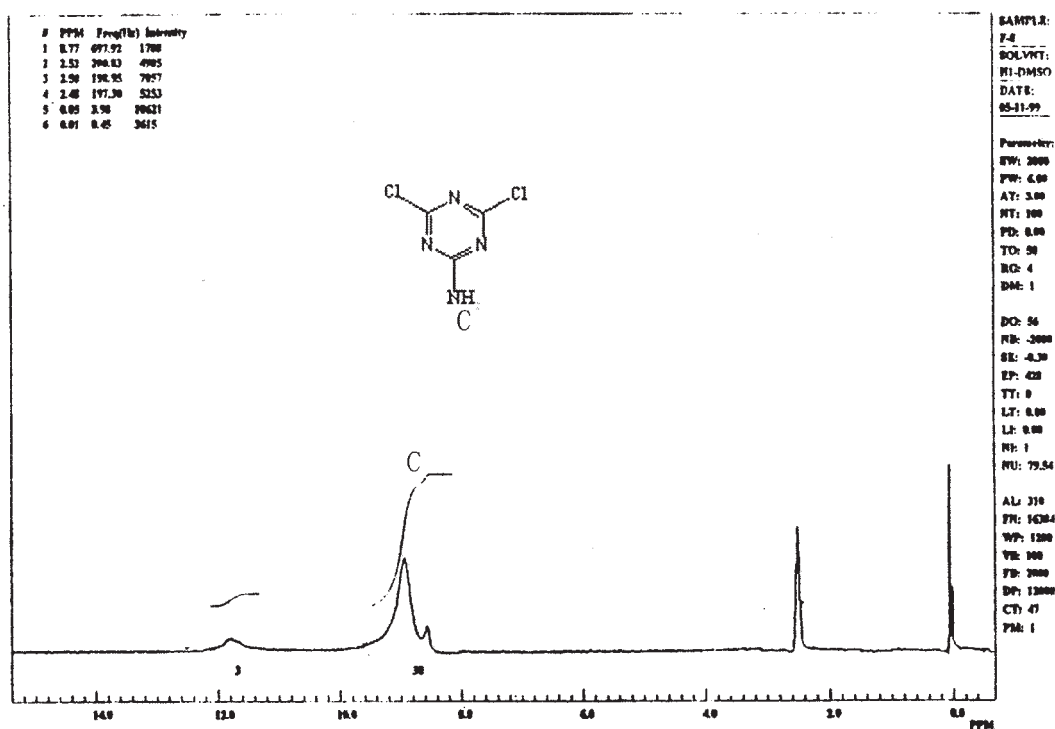**Figure 2**   The FTIR spectrum of monomer.
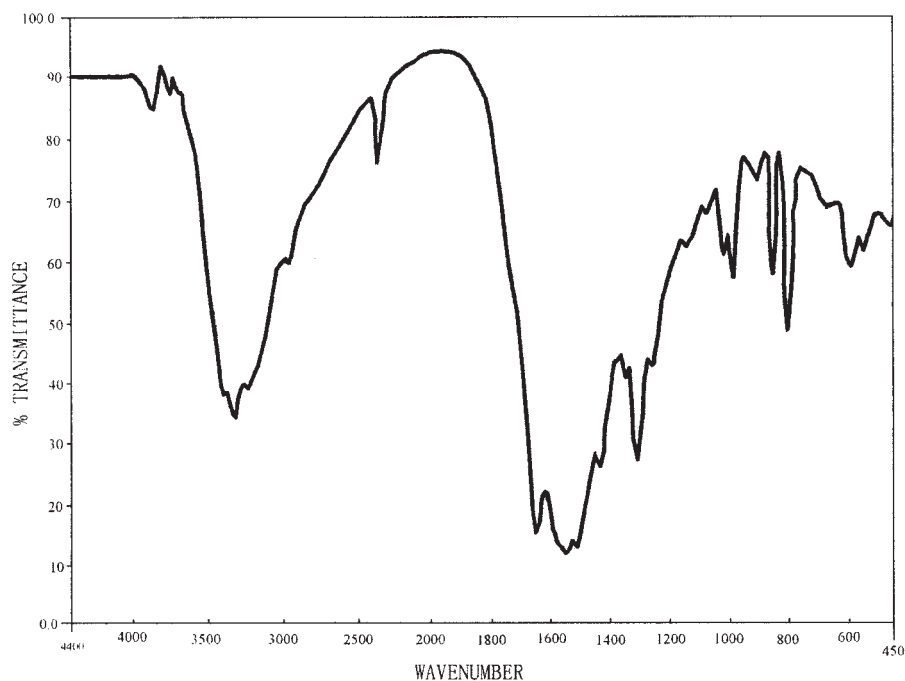

Figure 3   The ^{1}H-NMR spectrum of monomer.

Figure 4   The FTIR spectrum of CA.

served at 1175 and 1130 cm^{-1}, and the peak at 1306 cm^{-1} can be assigned to v_{tr-N} associated with the triazines ring; the peaks at 3316 and 1646 cm^{-1} can be assigned to N—H stretch and N—H bending in —NH$_2$, respectively. The peak at 3221 cm^{-1} was associated with the stretching mode of N—H in the —NH— group. No absorptions of v_{tr-Cl} at 993, 838,

and 534 cm^{-1} mean that the Cl atom attached on the triazine ring was totally replaced.[13]

The ^{1}H-NMR spectra of CA are illustrated in Figure 5. The characteristic multiplets between 6.54 and 6.62, which were clearly observed, were assigned to the eight protons **a** of two methylenes on main chain, but no resonances of —NH— and —NH$_2$ protons **b** ap-
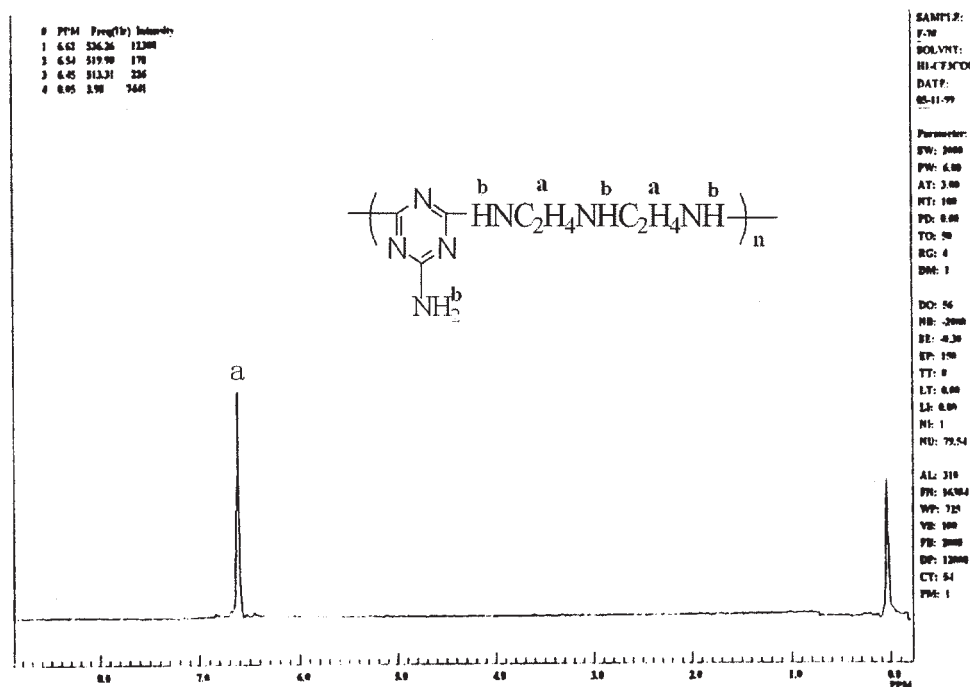

Figure 5 ^{1}H-NMR spectra of CA.

peared because of the addition of CF_3COOH. Table III lists the data of elemental analysis for CA. From Table III, it was seen that the calculated values were consistent with the found values.

Table IV depicts the N/P mole ratio and LOI values of the PE/IFR systems with the total loading of CA and APP additives kept a constant of 30 wt %. The LOI values of the system rapidly increase when CA was added into PE/APP systems, indicating that the CA is helpful to improve the flame retardancy of PE with the changing of N/P mole ratio. However, after the ratio of element N/P increases to 2.31/1, the LOI values decrease quickly with the increasing ratio of element N/P. It can be concluded that the increase of N concentration does not always mean better flame retardancy. In other words, there exists a distinct synergistic effect (SE) between element N and P.

CONCLUSION

A novel N-containing flame retardant, CA, was prepared successfully. The effects of various reaction conditions on the intrinsic viscosities of CA were investigated, and the optimal solution polycondensation conditions are as follows: reaction at 50°C for 30 min, then at 100°C for 2 h. The chemical structures of monomer and CA were confirmed by FTIR, MS, ^{1}H-NMR, and elemental analysis. The synthesized N-containing flame retardant has a significant promotion on the

TABLE III
The Data of Elemental Analysis for CA

Element	C	H	N
Calculated (%)	43.29	6.19	50.50
Found (%)	42.82	6.47	49.91

TABLE IV
Effect of IFR Composition on Flame Retardancy of PE with a 30 wt % Total Loading Level of the Additives

Composition of IFR-PE				
PE	APP	CA	N/P ratio in IFR (mol/mol)	LOI
70	30	0	—	22.6
70	25	5	1.75/1	29.5
70	22	8	2.31/1	31.2
70	20	10	2.79/1	27.0

flame-retardant behavior of PE when used together with APP.

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