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Abstract: *p*-Hydroxymethylbenzyl chloride was found to be an effective cross-linking agent for polystyrene. The reaction was found to occur by Friedel–Crafts alkylation between the benzyl alcohol/chloride functional groups in the additive and phenyl ring in polystyrene. The reaction was studied by TGA–IR to monitor the evolution of hydrogen chloride and water, and the structure of the resultant gel was analyzed by solid state NMR and elemental analysis. The potential application in flame-retardancy was evaluated using Cone calorimetry.

Keywords: Friedel-Crafts, Polystyrene, Fire retardancy, Cross-linking, Cone calorimetry

1. Introduction

One of the key steps in the burning of polymeric materials is the release of low molecular weight degradation products from the bulk to the vapor phase as the fuel source.[1] The strategy of cross-linking of polystyrene by Friedel–Crafts reaction has been studied to prevent or postpone this process to achieve thermal stabilization and flame retardancy.[2] The cross-linking temperatures of most systems that have been studied are lower than the processing temperature of polystyrene.[2–5] To increase the flame-retardancy of the system, the optimal cross-linking temperature should be higher than the processing temperature (ca. 200–250°C) to be practical and lower than degradation temperature (ca. 360°C) to be useful. Previous work from this laboratory has shown that the incorporation of functional groups (chloride, alcohol, etc.) by copolymerization, which subsequently form a cross-linked product through the Friedel–Crafts alkylation reaction and ultimately lead to the formation of char, is an effective way to stabilize polystyrene.[6–9]

We have previously reported on the study of multi-functional additives which could cross-link polystyrene at controllable temperature.[10] *p*-Hydroxymethylbenzyl chloride was found to be an effective cross-linking agent of polystyrene, and combined with

appropriate amount of catalyst precursor and inhibitor, the cross-linking temperature was in the desired range of above the processing temperature and below the degradation temperature. In this paper we report on the course of the reaction between *p*-hydroxymethylbenzyl chloride and polystyrene in the presence of both catalysts and inhibitors and the evaluation of the potential of this system for flame retardancy.

2. Experimental

2.1. Materials and instrumentation

Polystyrene (PS) was obtained from Aldrich Chemical Co., Mw ~ 280,000; high-impact polystyrene (HIPS) was supplied by Dow Chemical as Styron 404; acrylonitrile-butadine-styrene terpolymer (ABS) by Japan Synthetic Rubber Co., Ltd., containing 15 wt.% acrylonitrile, 40 wt.% butadiene, and 45 wt.% styrene; styrene-butadiene-styrene block copolymer (SBS) by Shell as Kraton D1102, containing about 75% butadiene; and K-resin by Phillips Petroleum as KR01, containing about 25% butadiene. The phosphate was provided by Solutia Inc., under trade name Santicizer 141, which consists of about 92% 2-ethylhexyl diphenyl phosphate (DPP). The sample of 2,2,6,6-tetramethyl-4-piperidinol (TMP) was obtained from the Aldrich Chemical Company.

2.2. Synthesis of 4-(hydroxymethyl)benzyl chloride (p-HMBC)[10]

The same preparative scheme as previously reported has been used for this synthesis.[10] This involves the reduction of 4-(chloromethyl)benzoyl chloride by sodium borohydride. The material was analyzed by mass spectroscopy and NMR spectroscopy and the spectroscopic results agree quite well with those previously reported.[11]

Samples for solid state NMR spectroscopy and elemental analysis were prepared by heating a quantity of the material under a nitrogen atmosphere in a glass tube to the desired temperature for 30 min. After cooling to room temperature, the samples were removed from the glass tubes and used for the analysis.

A type PL-2 Plasti-Corder Brabender mixer was used to make the blends; typical conditions were 180°C for 10 min. Samples for Cone calorimetry, etc., were prepared by compression molding in a heated Carver press. Elemental analysis was performed by Midwest Microlabs.

TGA–FTIR data was obtained using a Cahn TG-131 thermogravimetric analyzer interfaced to a Nicolet Magna 560 infrared spectrometer under inert atmosphere at a scan rate of 10°C/min. The mass of samples is in the range of 40–100 mg. Solid state NMR spectroscopy was carried out using a Bruker DX200 spectrometer operating at a frequency of 100 MHz for carbon. All experiments were carried out using cross polarization (CP) and magic angle spinning (MAS) at a frequency of 6 kHz. Spinning sidebands accounted for up to 16% of the total aromatic carbon. A recycle delay of 2 s was used for all experiments. The CP–MAS contact time was optimized at 1 ms for all experiments.

Cone calorimetry was performed per ASTM E 1354-92 using a Stanton Redcroft/PL Thermal Sciences instrument at 35 KW/m^2 in the horizontal orientation. The samples were 3 mm thick and mounted using the edge retainer frame and wire grid; the mass was approximately 32 g. Exhaust flow was set at 24 l/s and the spark was continuous until the sample ignited.

3. Results and discussion

3.1. Characterization of the degradation of a blend of p-hydroxymethylbenzyl chloride (p-HMBC) and polystyrene (PS) by TGA/FTIR

Based upon previous work on Friedel-Crafts chemistry on polystyrene, one would expect that an activated alkyl halide would alkylate the aromatic rings of polystyrene in a thermal reaction in the absence of a catalyst. This would actually be an autocatalytic reaction in that the evolved HCl would catalyze further reaction. One may further anticipate that in the presence of an amine, the evolved hydrogen chloride will be absorbed by the amine and the reaction will be retarded. Finally, the presence of a suitable catalyst should

accelerate the reaction. Most of these expectations were found to be true in an examination of the mixture by TGA/FTIR. The TGA and H_2O/HCl profiles of blend of polystyrene/p-HMBC/DPP/TMP are shown in Fig. 1. It is clear that the degradation occurs in two steps. The first step, 230–300°C, involves the loss of about 10% of the total mass and the evolved gases are water and hydrogen chloride. This confirms that the Friedel–Crafts reaction occurs in this temperature region, and it is clear that the Friedel–Crafts reaction is complete before the degradation of polystyrene commences. The second step of the degradation occurs between 360 and 480°C and involves the loss of about 85% of the mass. The products are the typical aromatic materials which arise from the degradation of polystyrene[12] and additional water is evolved. The evolution of water in this second step is only observed when DPP is present and, therefore, it is attributed to the dehydration of the diphenylphosphoric acid.
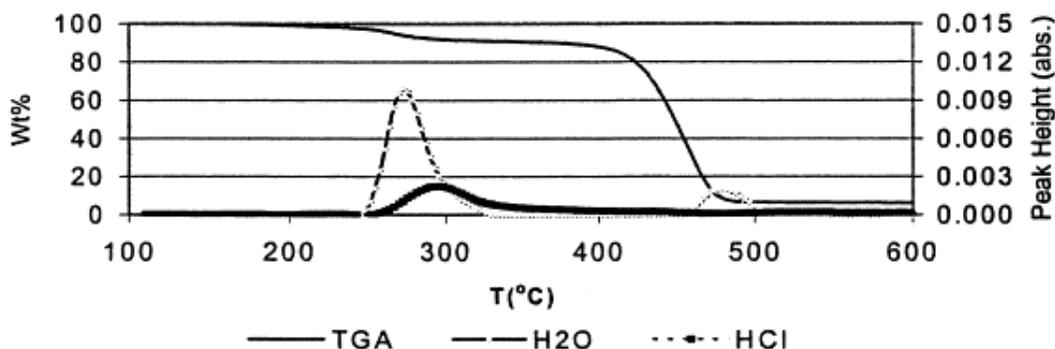

Fig. 1. TGA and H_2O/HCl profiles of blends of PS/HMBC/DPP/TMP.

The H_2O/HCl profiles of various blends are shown in Figs. 2 and 3 and the data concerning the onset of the evolution and the temperature at which the peak evolution is observed are collected in Table 1.
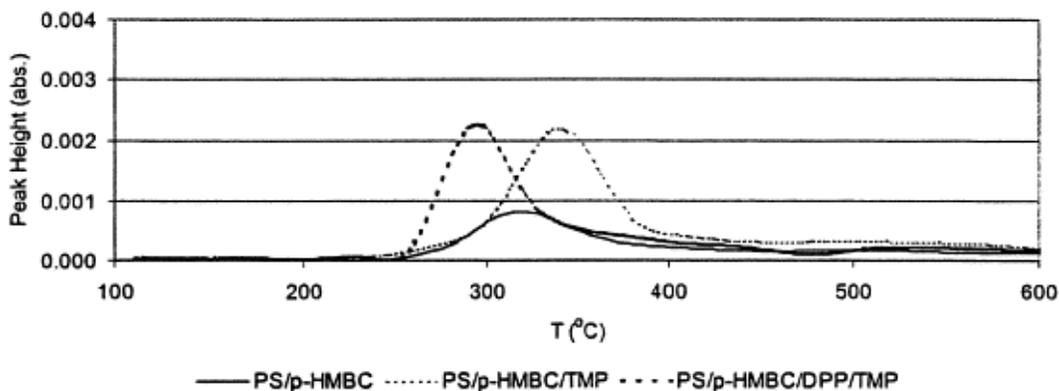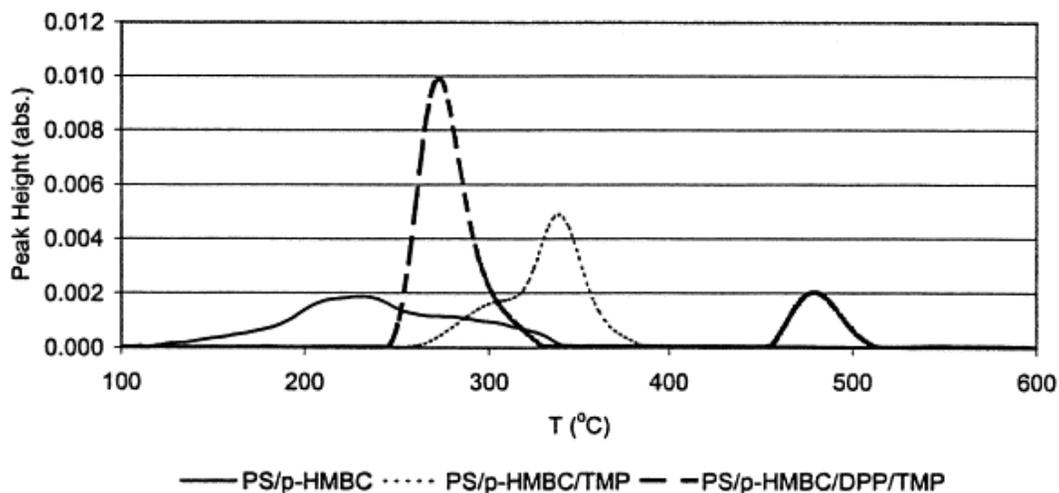
Fig. 2. HCl profiles of PS blends.

Fig. 3. H₂O profiles of PS blends.

Table 1. Evolution of water and hydrogen chloride from the mixtures of polystyrene and hydroxymethylbenzyl chloride alone and in the presence of additives

Sample	Onset temperature of the evolution (°C)	Peak temperature of the evolution (°C)
Evolution of hydrogen chloride		
PS+HMBC	150	320
PS+HMBC+TMP	260	340
PS+HMBC+TMP+DPP	250	290
Evolution of water		
PS+HMBC	130	230
PS+HMBC+TMP	260	340
PS+HMBC+TMP+DPP	245	270

One can see that in each case the onset temperature of the evolution is roughly comparable for both water and hydrogen chloride. It is somewhat difficult to define an onset temperature for the evolution of decomposition products. It is defined here as the temperature at which absorbance at that frequency characteristic of the evolved molecule begins to show substantial increase. The most likely explanation for these results is that a small amount of HCl is initially lost and this catalyzes the Friedel–Crafts reaction. In the presence of TMP the first molecules of HCl are absorbed by the amine and therefore the onset temperature of the gases (HCl and H_2O) is delayed since there is no catalyst present. When DPP is also present, the onset temperature is slightly lower and corresponds rather well to the temperature at which DPP undergoes degradation to give the acid catalyst.[7]

The peak shapes are quite different for the degradation in the absence of additives versus that in the presence of either only TMP or with both TMP and DPP. Integration of the area under the curve provides the information that approximately the same amount of water is lost in each case; the amount of HCl is also constant for all three cases. Thus the amount of gas evolved is not effected by the presence of the catalyst, but the temperature at which it is lost is effected. In order to compare the relative yields of H_2O and HCl, the observed spectroscopic intensities need to be normalized with respect to relative transition intensities, i.e. extinction coefficients. Due to the resolution of the instrument, each of the observed peaks corresponds to a convolution of multiple spectroscopic transitions. Spectral line intensities, corrected for temperature, were obtained for each individual spectroscopic transition. No correction was made for pressure broadening. For hydrogen chloride, the peak at 2727 cm^{-1} encompasses two individual peaks, one from each of the chlorine isotopes, and the summed spectral line intensities for these is 2.69×10^{-19} cm^{-1}/mol-cm^{-2}. For water, the peak at 3854 cm^{-1} was used and this band contains many individual transitions, when summed this gives a spectral line intensity of 4.02×10^{-19} cm^{-1}/mol-cm^{-2}.[13] If one divides the observed intensities by the sum of the appropriate spectral line intensity factors, there is approximately 1.07 mol of water evolved for every mol of HCl evolved. Considering the experimental uncertainties in the absorbances and the approximations

in the extinction coefficients, this may be considered to indicate that the same amount of each gas is evolved.

The best explanation of these results is that the chloride and alcohol portions of the molecule have an equal possibility of undergoing the Friedel–Crafts reaction. This leads to a functionalized polystyrene in which some of the aromatic rings that have been alkylated possess an alcohol functionality while others have a chloride functionality. Once the polystyrene is alkylated, the mobility of the new functionalized polymer is greatly diminished. A significantly higher temperature is required for this functionalized polymer to encounter and then alkylate a new ring to produce a cross-linked polymer. The evolution of both H_2O and HCl occurs over a temperature range which varies between more than 300°C in the widest to somewhat more than 100°C at the narrowest. This is depicted below in Scheme 1.
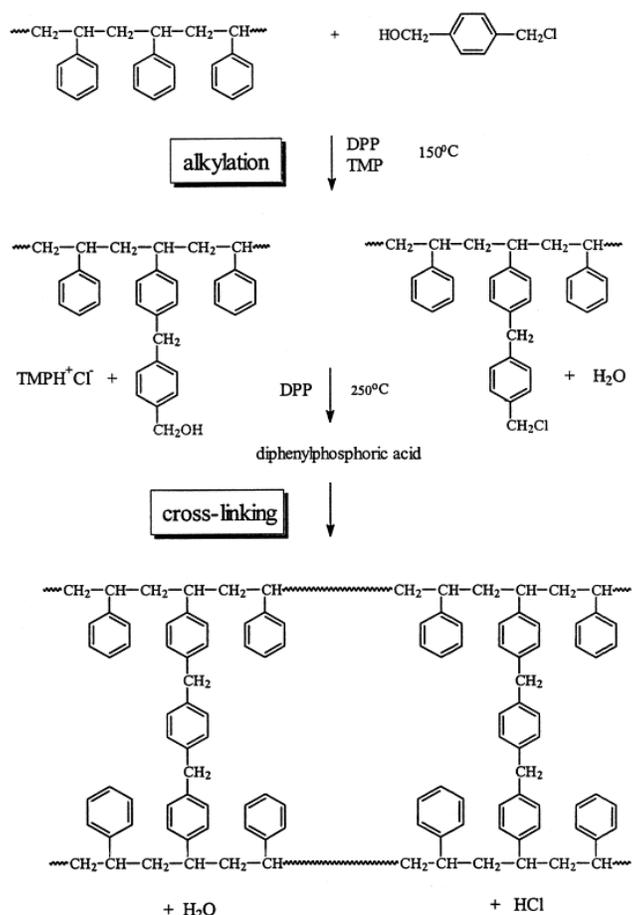
Scheme 1. Alkylation and cross-linking of polystyrene with HMBC in the presence of TMP and DPP as catalyst.

3.2. Characterization of the functionalized and cross-linked structure

A blend of polystyrene, the alkylating agent, and the amine was prepared by solution mixing and then characterized by elemental analysis and solid state NMR spectroscopy. The elemental analysis results are shown in Table 2. One sees that alkylation occurs at 200°C and that somewhat more of the oxygen reacts initially than does the chloride but at 250°C more of the chloride is lost than the oxygen. After 5 h at 300°C all of the chloride and the alcohol have been lost and a cross-linked matrix is obtained. The mixture after heating at 200°C is completely soluble and thus only alkylation has occurred, without cross-linking. At higher temperatures insolubility results which indicates that a cross-linked structure has been produced.

Table 2. Elemental analysis of blends of PS, HMBC and TMP as a function of heating

Sample no.	T (°C)	Time (h)	C (%)	H (%)	Cl (%)	O (%)
1	–	0	89.21	7.50	2.23	1.02
2	200	0.5	89.50	7.62	1.99	0.71
3	250	0.5	90.46	7.72	1.12	0.60
4	300	0.5	91.71	7.70	0.49	0.05
5	300	5.4	92.34	7.67	~0	~0

3.3. Solid state NMR

The same samples which were analyzed by elemental analysis were also subjected to solid state ^{13}C-NMR analysis; the spectra as a function of temperature are shown in Fig. 4. Initially one observes two peaks in the aromatic region, which may be assigned to the non-protonated and protonated carbons of both polystyrene and HMBC, and a broad peak in the aliphatic region, attributable to the methylene and methine carbons. It is only at 400°C, and higher temperature, that a change is apparent in the spectrum. The first observation that may be made is the increased width of the peaks, indicative of chain rigidity due to a high cross-link density. One can also observe that both the aromatic and the aliphatic peaks have decreased in intensity with the aliphatic carbon peaks disappearing much faster than the aromatic carbon peaks. This is indicative of the charring reaction which

occurs at high temperatures. In previous work we have reported on a radiative gasification experiment in which one is able to degrade the polymer in a nitrogen atmosphere and, using a video camera, record the degradation process. In these experiments we observed the charring process for a related system.[8]
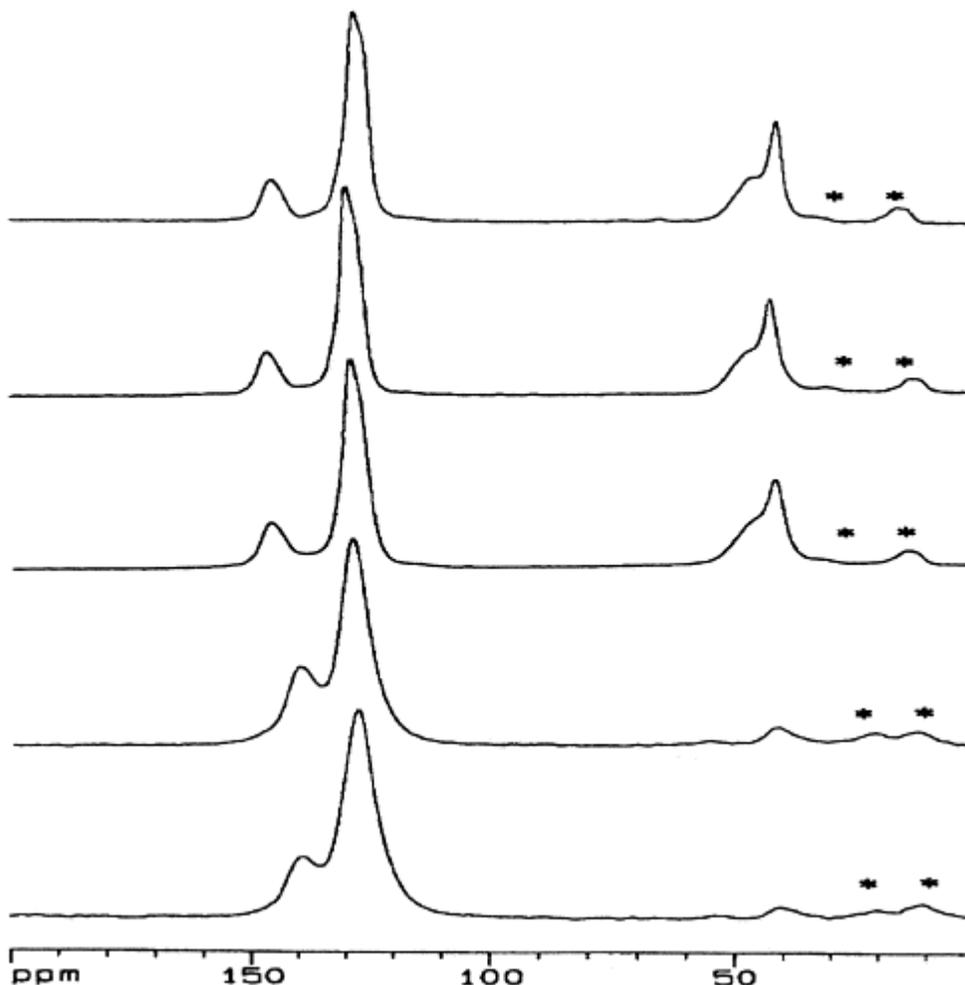
Fig. 4. Solid state NMR of blends of polystyrene and *p*-HMBC, after treatment at: (a) no treatment, (b) 300°C, 0.5 h, (c) 300°C, 5.4 h, (d) 400°C, 1/2 h, (e) flame treatment in air, 0.1 h. Spinning sidebands are indicated by *.

3.4. Evaluation of flame retardancy

The flame retardancy of multi-functional additives was evaluated by Cone calorimetry and the results are presented in Table 3. The total energy that is released is not shown in the table but it is quite comparable for all samples and this indicates that a

condensed phase process is occurring in all cases. Discussing all of the parameters in turn one finds that the time to ignition is adversely effected by the presence of the additives while the time to burnout may be slightly increased. It is very significant to note the significant reduction in the peak heat release rate, PHRR; the greatest reduction occurs for the combination of HMBC in the presence of both the amine and the catalyst but a reduction is observed in all cases. This change is shown in Fig. 5, which includes the peak heat release rate data for the virgin polymers and their blends with HMBC and the two necessary additives to affect the most efficacious reaction. Likewise there is always a reduction in the mass loss rate and the fraction of mass which is lost at burnout is always lower in the presence of the amine and catalyst. Finally we note that the extinction area, and the specific extinction area, both of which are a measure of smoke formation, do not change significantly for any system. This means that additional smoke is not generated by these systems. It must be noted that all these samples give no rating in the UL-94 test. If the loading of HMBC is increased to 20% a V-2 rating is possible. Further work will be performed using this system, which is quite efficacious in reducing the rate of heat release, with other additives designed to reduce the ignitiability of the polymer.

Table 3. Cone calorimetric data for various systems at 35 kW/m^2 heat flux

Polymer	Cross-linking agent (CRA)	CRA/TMP/DPP	Time to ignition (s)	Time to burnout (s)	PHRR (kW/m^2)	Time to PHRR (s)	Mass loss rate, (mg/s)	Mass loss at burnout (%)	Extinction area (m^2)
PS	–	–/–/–	50	222	747	185	162	83	37
PS	HMBC	10.0/.10/0	25	228	520 (29)	195	148	90	46
PS	HMBC	10.0/.10/5.0	30	240	365 (51)	115	112	63	51
PS	DCPX	10.0/.10/0	35	225	570 (24)	195	154	87	47
PS	DCPX	10.0/.10/5.0	35	220	512(31)	175	165	83	56
HIPS	–	–/–/–	75	231	916	190	184	83	39
HIPS	HMBC	10.0/0/5.0	35	240	352 (62)	220	108	70	47
HIPS	HMBC	10.0/.10/5.0	25	240	348 (62)	80	101	57	66
HIPS	DCPX	10.0/0/5.0	35	225	532 (42)	150	159	83	52
HIPS	DCPX	10.0/.10/5.0	–	226	526 (43)	180	152	80	58
HIPS	Diol	20.0/0/5.0	–	240	315 (66)	120	93	60	54
ABS	–	–/–/–	–	187	1195	150	262	87	26
ABS	HMBC	10.0/.10/5.0	–	203	675 (44)	140	178	86	52
ABS	DCPX	10.0/.10/5.0	–	209	715 (40)	140	178	86	57
SBS	–	–/–/–	–	158	1368	135	256	84	41
SBS	HMBC	10.0/.10/5.0	–	143	1131 (17)	130	271	85	45
SBS	DCPX	10.0/.10/5.0	–	134	1110 (19)	105	269	85	49
K-resin	–	–/–/–	50	166	754	185	302	81	80

Polymer	Cross-linking agent (CRA)	CRA/TMP/DPP	Time to ignition (s)	Time to burnout (s)	PHRR (kW/m²)	Time to PHRR (s)	Mass loss rate, (mg/s)	Mass loss at burnout (%)	Extinction area (m²)
K-resin	HMBC	10.0/.01/5.0	–	215	588 (22)	185	164	84	54
K-resin	DCPX	10.0/.10/5.0	–	195	647 (14)	160	200	88	50
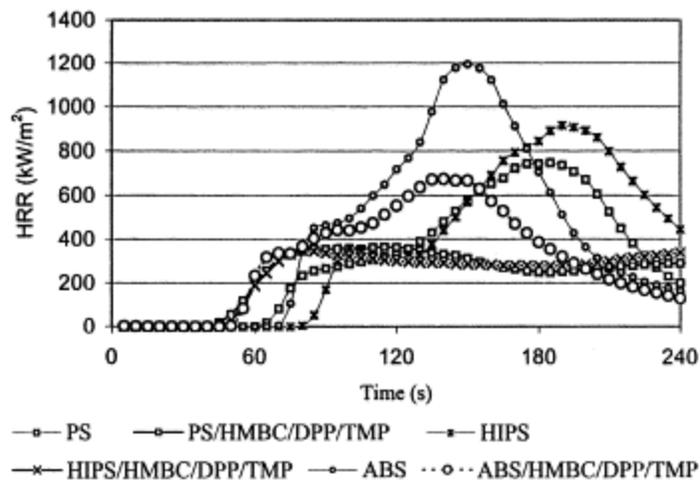
Fig. 5. Heat release rate of cone calorimetry of styrenic polymers and their blends.

4. Conclusions

The reaction proceeds most smoothly when two additives, a phosphate ester and a hindered amine are present. The hindered amine functions as a base to consume the hydrogen chloride liberated by the first alkylation, thus removing a catalyst which would facilitate cross linking at a relatively temperature to produce an acid catalyst, which can then function as the cross linking catalyst, as desired, at this higher temperature.

Acknowledgements

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