

Phosphorus-Containing Polyisocyanurate Elastomers for Flame Retardant Application

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Phosphorus-Containing Polyisocyanurate Elastomers for Flame Retardant Application

Yunfei Guo, Julian Kleemann, Rint P. Sijbesma,* and Željko Tomović*

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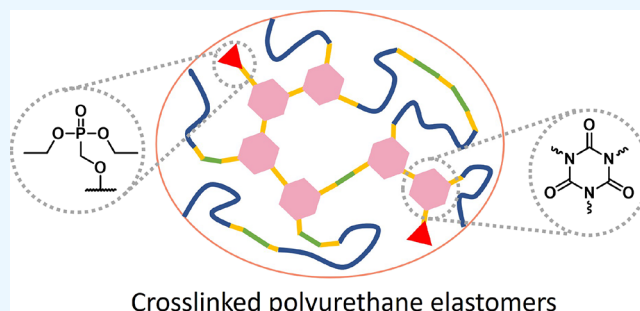
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ABSTRACT: Polyurethane (PU) is one of the most common and versatile polymers in many applications especially in the construction and automotive industry where the improvement of thermal stability and flame retardancy is crucial. As polyisocyanurate (PIR) is well known to have a high decomposition temperature and phosphorus motifs are usually used as flame retardants in polymers, the introduction of PIR and phosphorus motifs in polyurethanes can lead to PUs with high thermal stability and flame retardancy. We investigated a synthetic pathway to introduce polyisocyanurate (PIR) and phosphorus motifs in polyurethanes via co-trimerization of 4,4'-methylene diphenyl diisocyanate (4,4'-MDI) and monoisocyanate, which was synthesized from the reaction between diethyl (hydroxymethyl)phosphonate (DEHP) and 4,4'-MDI. The resulting PIR-DEHP prepolymer was used to prepare PIR-DEHP elastomers in both solvent and solvent-free conditions. The elastomer with polyester polyol and 15 wt % 1,4-butanediol in the polyol component showed high char formation (25.5 wt %) and 55% reduction in the total heat release (THR) relative to the reference elastomer without PIR and phosphorus content. It is expected that the use of the PIR-DEHP prepolymer can be extended to other applications, such as rigid PU foams and compact thermosets where the flame retardancy and bulk reaction conditions are required.

KEYWORDS: polyurethane, polyisocyanurate, phosphorus, flame retardancy, trimerization



1. INTRODUCTION

Polyurethane (PU) is one of the most versatile polymers and it is used to provide materials with a wide range of chemical, thermal, and mechanical properties.^{1–5} Although many different PU materials are available, further improvement of the physical properties, especially thermal stability and flame retardancy, will make them suitable for an increased number of applications and meet the new market demands. The introduction of polyisocyanurate (PIR) and phosphorus motifs in polyurethanes can lead to PUs with better thermal properties as polyisocyanurate is well known to have a high decomposition temperature and phosphorus motifs are usually used as flame retardants in polymers.^{6–10} However, the brittleness of PIR networks and the limited compatibility of phosphorus motifs with the PUs are challenges that need to be improved.

PIRs are widely applied in PU elastomers in order to improve their thermal stability and flame-retardant properties.^{6,7} These elastomers are generally obtained via one of the two most common synthesis routes.^{11–16} They can be prepared by trimerization of an isocyanate prepolymer that is obtained from the reaction of excess isocyanates and polyols (Scheme 1a) or via the in situ reaction of isocyanates, polyols, and chain extenders in the presence of a trimerization catalyst

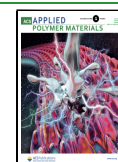
(Scheme 1b). However, both of the synthesis routes lead to PU materials with relatively low PIR content due to a rapid increase of the network density and viscosity and restricted catalyst diffusion in the reaction mixture.

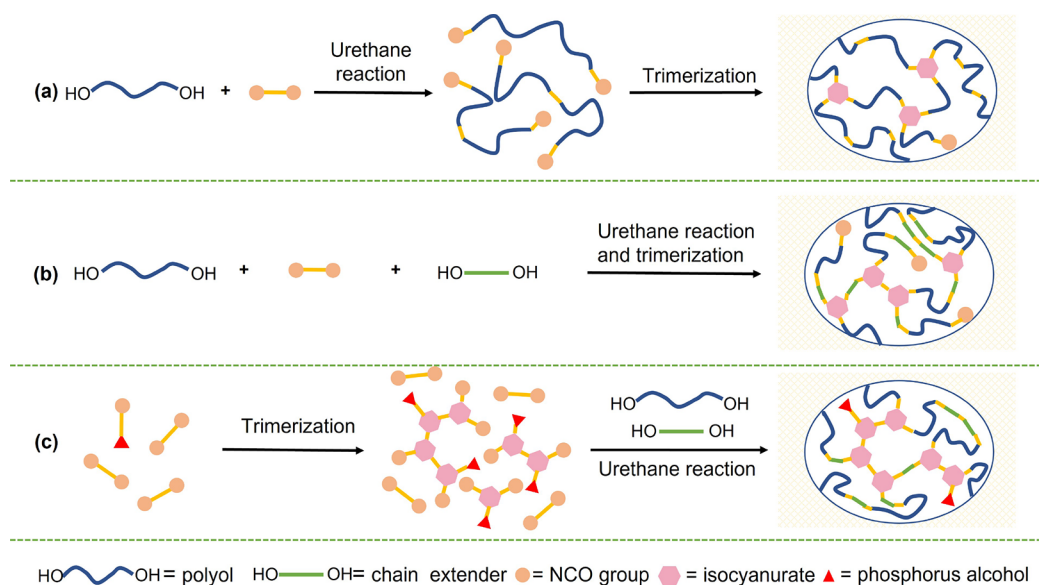
A promising way to develop a flexible network with a high concentration of PIR structures is to synthesize a PIR-containing isocyanate prepolymer via co-trimerization of mono- and difunctional isocyanates (Scheme 1c).^{17–21} In this way, the cross-link density of the PIR prepolymer is more controllable and the flexibility of the network is tunable. In addition, the liquid PIR prepolymer can be prepared via this synthetic way and it provides the possibility to prepare PIR elastomers in both solvent and solvent-free conditions. However, the commercially available monofunctional isocyanates, such as butyl and phenyl isocyanates, are too volatile and toxic to be used in large-scale industrial applications. As an alternative approach, monofunctional isocyanates can be

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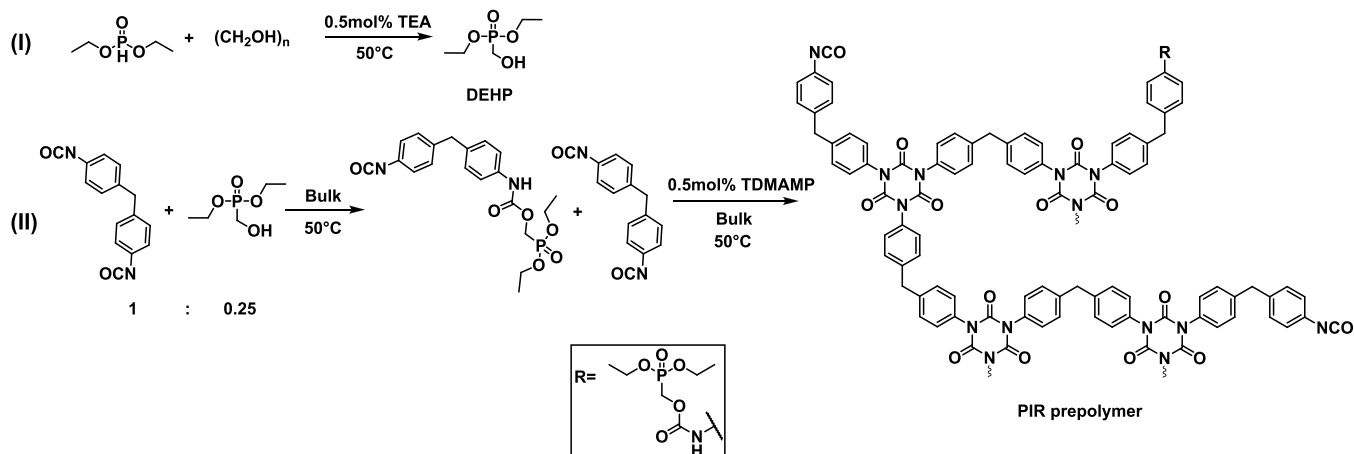
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Scheme 1. Two Most Common Synthesis Pathways to Prepare PIR Elastomers and Preparation of the PIR Elastomer in This Work^a


^a(a) Trimerization of the isocyanate prepolymer obtained from the reaction between the excess of isocyanates and long-chain polyols; (b) in situ reaction of isocyanate, polyols, and chain extenders in the presence of the trimerization catalyst; and (c) urethane reaction of the PIR prepolymer with polyols and chain extenders.

Scheme 2. Synthesis of DEHP (I) and the PIR-DEHP Prepolymer (II)


synthesized in situ by reacting monofunctional alcohols with diisocyanates and used in subsequent co-trimerization with diisocyanates to form PIR networks.

Although phosphorus-containing compounds are well known as flame retardants, which are typically added in polyurethanes as fillers or additives,^{22–29} they may leach out or migrate to the sample surface, leading to the deterioration of the mechanical properties of the materials. In order to improve the compatibility of phosphorus compounds, phosphorus-containing polyols have been synthesized and introduced into PU materials via covalent bonds.^{23,30–35} The flame retardancy can be realized via condensed and gas-phase mechanisms, and many phosphorus-containing compounds utilize both.^{23,25,36,37}

In the condensed phase, many phosphorus flame retardants mediate the formation of char, which reduces the release of volatiles. Some phosphorus flame retardants also give intumescence, which produces a protective layer and slows down heat transfer to the underlying material. In parallel with

condensed-phase mechanisms, phosphorus compounds also act as flame retardants in the gas phase, which significantly improves the flame retardancy of the materials. It is generally accepted that PO· radicals formed from phosphorus-containing compounds play an important role to provide flame retardancy. During combustion, OH· radicals are replaced by PO· radicals, which are formed from the decomposition of phosphorus flame retardants. The PO· radicals are less reactive, thus slowing down or interrupting the oxidation of hydrocarbons. Therefore, the addition of phosphorus-containing motifs can be used to inhibit flames and reduce the heat production upon combustion, which enhances the flame retardancy of the material.

This work aims to combine both PIR and phosphorus motifs in PU elastomers in order to enhance the intrinsic thermal stability and flame retardancy of these materials. First, a monofunctional phosphonate alcohol, namely, diethyl (hydroxymethyl)phosphonate (DEHP), was synthesized and

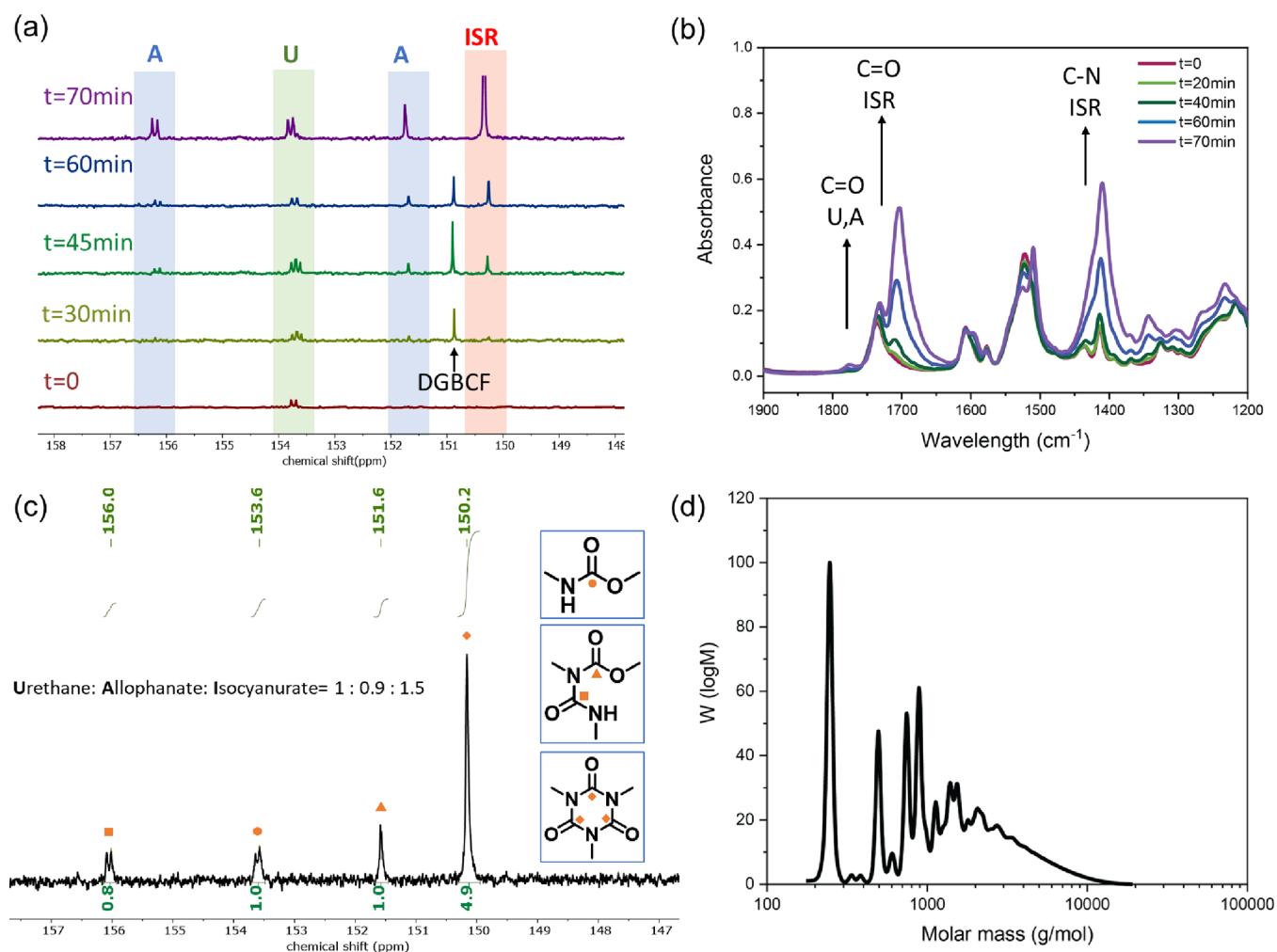


Figure 1. (a) ^{13}C NMR spectra (acetone- d_6) and (b) FT-IR spectra of co-trimerization of mono- and difunctional isocyanates. (c) Quantitative ^{13}C NMR spectrum (acetone- d_6) of the PIR-DEHP prepolymer. The ratio of U:A:ISR was determined by integrals of the carbonyl carbon peaks: U (urethane), A (allphanate), and ISR (isocyanurate). (d) GPC trace of the PIR-DEHP prepolymer.

introduced into a PIR matrix by reacting with 4,4'-methylene diphenyl diisocyanate (4,4'-MDI) in a 0.25:1 molar ratio to produce a mixture containing both mono- and di-isocyanates. Then, the mixture was trimerized and quenched by acid before solidification in order to get the liquid PIR-DEHP prepolymer. Finally, PIR-DEHP elastomers were prepared by reacting the PIR-DEHP prepolymer and long-chain polyols with different amounts of 1,4-butanediol as a chain extender in both solution and bulk conditions. The combination of PIR and phosphorus motifs led to enhanced flame-retardant properties of PU materials based on the initial cone calorimetry measurement. This promises the potential use of the PIR-DEHP network in various polyurethane applications such as rigid foams, compact elastomers, thermosets, and adhesives where flame retardancy is required. Our approach helps improve the intrinsic flame retardancy of PU materials and reduce the use of classical flame-retardant additives.

2. RESULTS AND DISCUSSION

2.1. Preparation of the PIR-DEHP Prepolymer.

Monofunctional phosphonate alcohol diethyl (hydroxymethyl)phosphonate (DEHP) was synthesized from diethyl phosphite and paraformaldehyde with triethylamine as a catalyst (Scheme 2-I and Figures S1 and S2).³⁸ After the

reaction, pure DEHP was obtained by evaporation of the triethylamine under reduced pressure.

To maximize the phosphorus content and keep the viscosity low enough to perform trimerization in bulk afterward, 4,4'-MDI and DEHP were reacted in a molar ratio of 1:0.25, resulting in an isocyanate mixture with 75 mol % difunctional isocyanate and 25 mol % monofunctional isocyanate (Figure S3).

The trimerization of di- and monofunctional isocyanate mixtures was carried out in bulk at 50 °C using 2,4,6-tris(dimethylaminomethyl)phenol (TDMAMP) as the trimerization catalyst (Scheme 2-II). As soon as the viscosity increased strongly, the reaction was quenched by diethylene glycol bis-chloroformate (DGBCF) (Figure S4). The formation of isocyanurate was monitored with both ^{13}C NMR spectroscopy at 150.1 ppm (carbonyl carbon) (Figure 1a)^{39,40} and with FT-IR at 1704 cm^{-1} (C=O stretching) and 1410 cm^{-1} (C-N stretching) (Figure 1b).⁴¹ After reaction, the urethane (U), allphanate (A), and isocyanurate (ISR) ratio in the PIR-DEHP prepolymer was further determined by ^{13}C NMR spectroscopy. In order to allow quantitative integration of the carbonyl peaks, 25 s of a relaxation delay was required and chromium(III) acetylacetonate ($\text{Cr}(\text{acac})_3$) was used as a relaxation agent.^{42–44} In the quantitative ^{13}C NMR spectrum

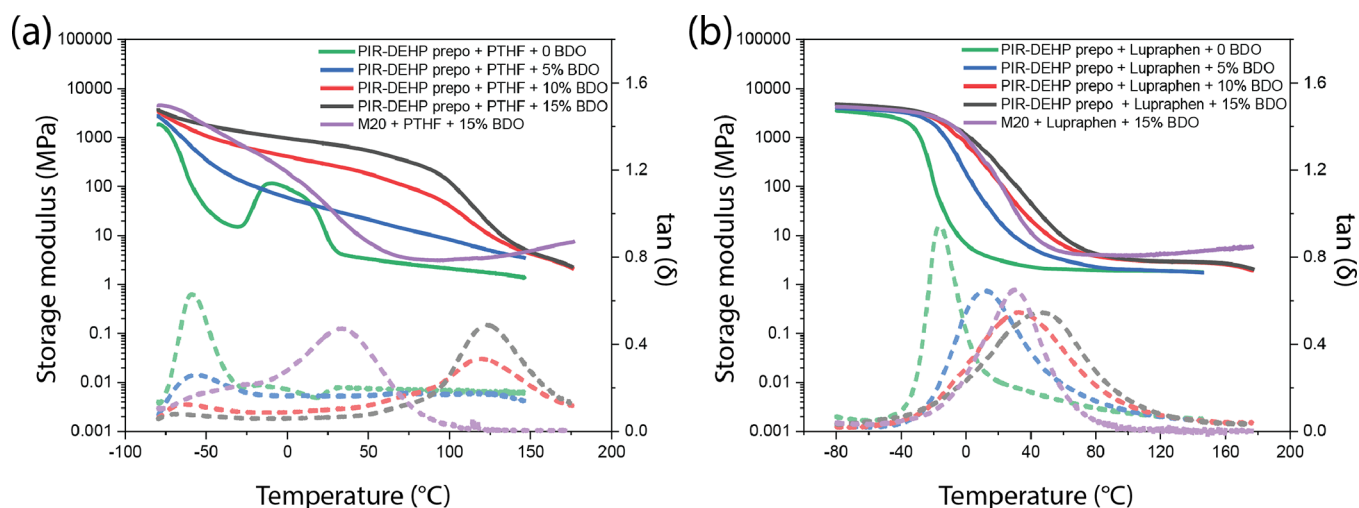


Figure 2. DMA curves of (a) PTHF-containing and (b) Lupraphen-containing PIR-DEHP and M20 elastomers with different amounts of BDO. Solid line: storage modulus; dashed line: $\tan(\delta)$.

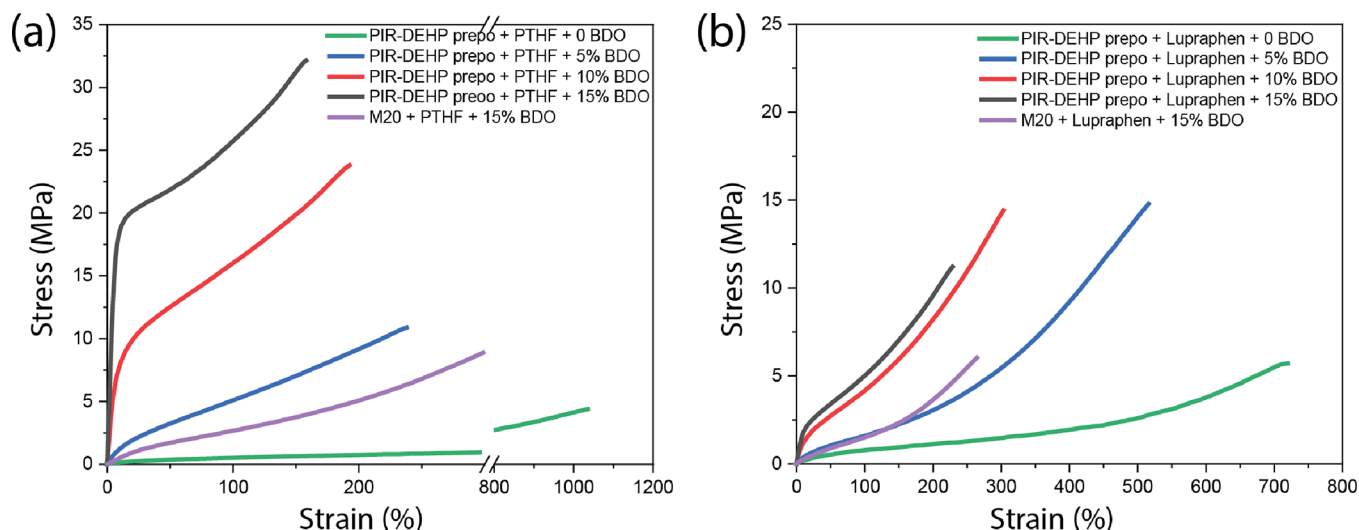


Figure 3. Tensile test of (a) PTHF-containing and (b) Lupraphen-containing PIR-DEHP and M20 elastomers with different amounts of BDO.

shown in Figure 1c, the peaks at 153.6, 151.6, 156.0, and 150.2 ppm were assigned to carbonyl carbon atoms of urethane, allophanate (two peaks), and isocyanurate respectively.^{39,40} The molar ratio of urethane:allophanate:isocyanurate (U:A:ISR) was calculated as 1:0.9:1.5 based on the integrals of carbonyl carbon peaks. In addition, an NCO content of 14.5 wt % was determined by back-titration and the average molar mass of the PIR-DEHP prepolymer, that is, 710 g/mol, was determined with GPC (Figure 1d) from which the average functionality of the PIR-DEHP prepolymer was calculated to be 2.5 via the following equation

$$f_n = \frac{\text{NCO content} \times M_{\text{prepolymer}}}{M_{\text{NCO}} \times 100 \text{ wt}\%} = \frac{14.5 \text{ wt}\% \times 710 \text{ g/mol}}{42 \text{ g/mol} \times 100 \text{ wt}\%} = 2.5 \quad (1)$$

where $n_{\text{prepolymer}}$ is the mole amount of the prepolymer, M_{NCO} is the molecular weight of the NCO group, and $M_{\text{prepolymer}}$ is the number average molecular weight of the prepolymer.

2.2. Preparation and Characterization of Solution Cast PIR-DEHP Elastomers. The PIR-DEHP elastomers

were prepared by the reaction of the PIR-DEHP prepolymer with commercially available polyether polyol or polyester polyol with an average molecular weight of 2000 g/mol such as PolyTHF 2000 (PTHF) and Lupraphen 6601/2 (Lupraphen) and various amounts of 1,4-butanediol (BDO) as a chain extender (0, 5, 10, or 15 wt % in the polyol component). The molar ratio of NCO:OH was kept constant at 1.05 (index 105),^{45,46} and the elastomers were solution-cast from THF (Table S1). The PIR-DEHP elastomers prepared with PTHF were turbid white, and those with Lupraphen were transparent (Figure S6).

Commercially available polymeric MDI, namely, Lupranate M20 (M20), which has a slightly higher functionality of 2.7, was also used to prepare M20-based elastomers as reference materials. M20 was reacted with either PTHF or Lupraphen polyol and 15 wt % BDO in the polyol component under the same casting conditions used for PIR elastomers (Table S1).

The dynamic mechanical analysis (DMA) of the elastomers is shown in Figure 2 and Table S2. Together with the turbidity of the PTHF-containing PIR-DEHP elastomers, phase separation is confirmed by the presence of two T_g 's in the elastomers. The lower T_g is strongly influenced by the T_g of

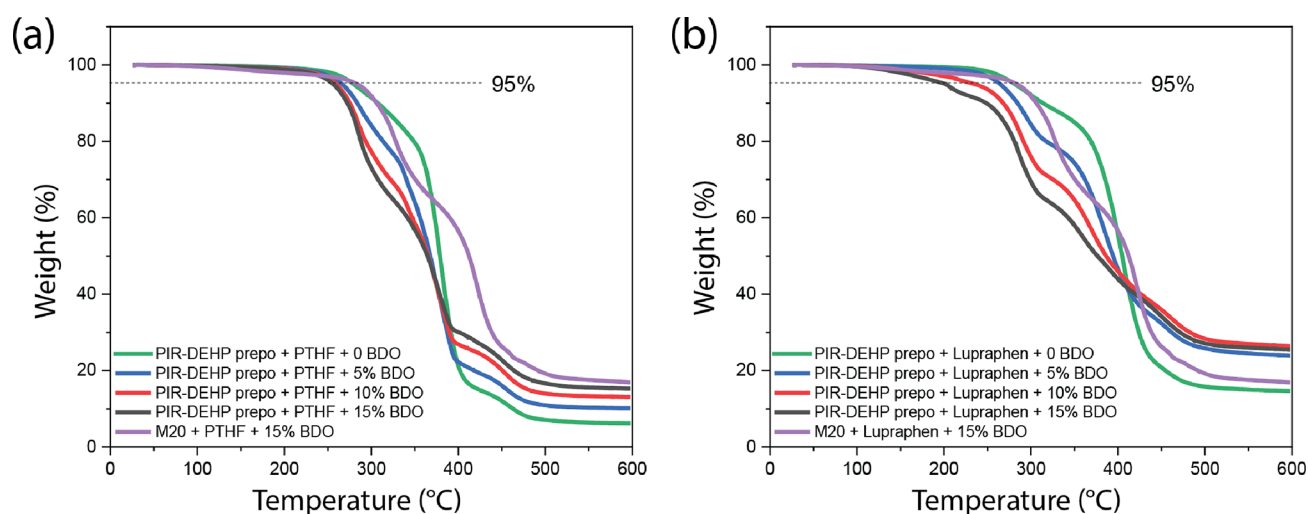


Figure 4. TGA curves of (a) PTHF-containing and (b) Lupraphen-containing PIR-DEHP and M20 elastomers with different amounts of BDO.

Table 1. TGA Measurement Data of PTHF-Containing and Lupraphen-Containing PIR-DEHP and M20 Elastomers with Different Amounts of BDO

| PTHF | | | | | Lupraphen | | | | |
|--------------------|--------------------------------------|---------------|----------------|--------------------|--------------------|--------------------------------------|---------------|----------------|--------------------|
| BDO content (wt %) | aromatic content ^a (wt %) | T_{d5} (°C) | T_{d10} (°C) | char formation (%) | BDO content (wt %) | aromatic content ^a (wt %) | T_{d5} (°C) | T_{d10} (°C) | char formation (%) |
| PIR elastomers | | | | | | | | | |
| 0 | 20 | 279.5 | 307.5 | 6.2 | 0 | 20 | 281.2 | 313.7 | 14.7 |
| 5 | 33 | 266.3 | 283.8 | 10.1 | 5 | 33 | 264.5 | 284.5 | 24.0 |
| 10 | 42 | 259.3 | 275.3 | 13.1 | 10 | 42 | 234.9 | 268.1 | 26.4 |
| 15 | 48 | 256.1 | 272.5 | 15.3 | 15 | 48 | 201.8 | 248.6 | 25.5 |
| M20 elastomers | | | | | | | | | |
| 15 | 37 | 283.7 | 306.2 | 17.0 | 15 | 37 | 218.2 | 284.3 | 16.3 |

^aThe aromatic content is calculated based on the weight percentage of aromatic isocyanate in the elastomers.

PTHF polyol, and the higher T_g at approximately 120 °C is influenced by the T_g of PIR structures. When there was no BDO in the elastomer, cold crystallization with subsequent melting of PTHF was found between −29 and 35 °C (green curve).⁴⁷ The addition of BDO limited the crystallization tendency of PTHF, and thus no cold crystallization peaks were found in the curves of elastomers containing BDO. For the Lupraphen-containing PIR-DEHP elastomers, only one narrow $\tan(\delta)$ peak was observed, which indicates that the PIR structures have good compatibility with polyester polyol. The T_g of the elastomers increased with the increasing amount of PIR structures as well as aromatic content. Compared to the M20 elastomers, PIR-DEHP elastomers had a higher T_g as they contained PIR structures and had a higher aromatic content.

The mechanical properties of the PIR-DEHP elastomers with different amounts of BDO as well as the M20 elastomer containing 15 wt % BDO in the polyol component were measured by a tensile test (Figure 3 and Table S3). The PIR-DEHP elastomers became stiffer with higher isocyanurate content. As a result, the stress at break and the Young's modulus increased, while the elongation at break decreased. The M20 elastomers, which contain no isocyanurate, had lower stress at break and lower Young's modulus. This could also be explained by the lower T_g of M20 elastomers with either PTHF or Lupraphen polyol and 15 wt % BDO, which was approximately room temperature (34 and 18 °C,

respectively); thus, the materials were more rubbery and easier to break than the isocyanurate-containing materials.

Finally, thermogravimetric analysis (TGA) of these elastomers was measured (Figure 4). The decomposition temperatures at 5% weight loss (T_{d5}), 10% weight loss (T_{d10}), and char formation at 596 °C are shown in Table 1. The T_{d5} and T_{d10} are mainly dependent on the decomposition of urethane bonds and decrease with higher BDO content. For PTHF-containing PIR-DEHP elastomers, with more BDO, the amount of isocyanurate structures as well as aromatic content increased, leading to higher char formation. The char formation of Lupraphen-containing elastomers was higher than PTHF-containing elastomers, but it did not significantly change with the amount of BDO. Nevertheless, all PIR-DEHP elastomers showed higher char formation than classical 4,4'-MDI-based elastomers, which were synthesized from 4,4'-MDI, polyol, and BDO without trimerization (Figure S7 and Table S4). With PTHF and 15 wt % BDO, M20 elastomers had slightly higher char formation than PIR-DEHP elastomers. However, with Lupraphen and the same amount of BDO (15 wt %), the char formation of PIR-DEHP elastomers was much higher than M20 elastomers.

2.3. Flame Retardancy of PIR-DEHP Elastomers. As the PIR-DEHP prepolymer is still a liquid, it is also possible to use this prepolymer to cast elastomers without solvent, which is advantageous for industrial applications. To study the flame retardancy of the elastomers, three samples were prepared using Lupraphen as the polyol due to the high char formation

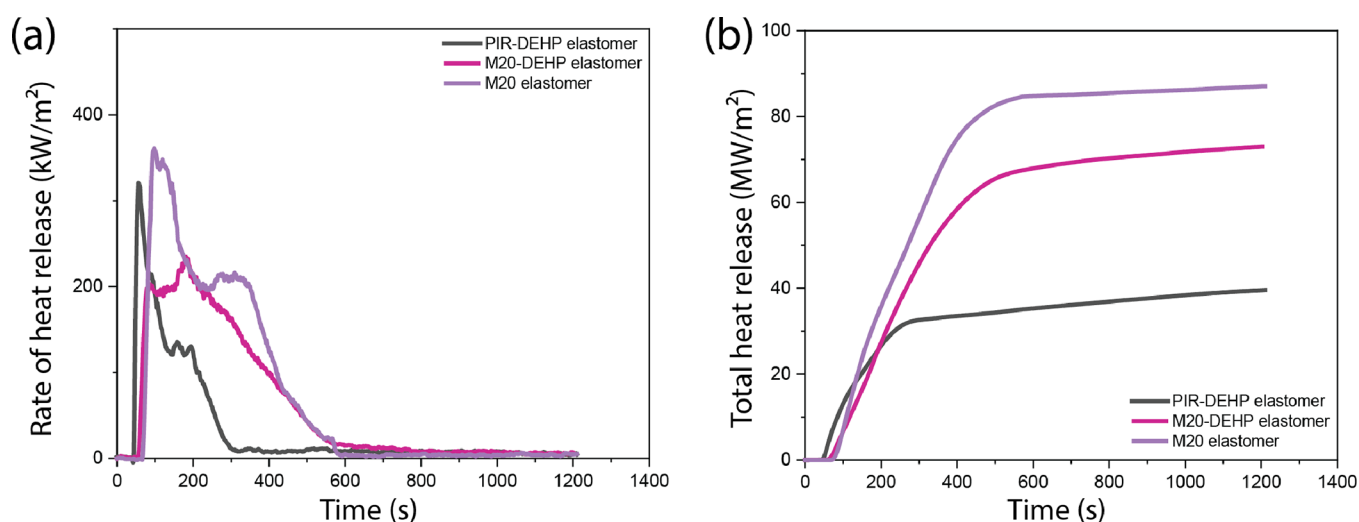


Figure 5. (a) HRR and (b) THR curves of PIR-DEHP, M20-DEHP, and M20 elastomers measured by a cone calorimeter under a heat flux of 35 kW/m².

Table 2. Cone Calorimetry Results of PIR-DEHP, M20-DEHP, and M20 Elastomers Measured under a Heat Flux of 35 kW/m²

| sample | TTI (s) | PHRR ^a (kW/m ²) | <i>t_p</i> (s) | THR (MJ/m ²) | AEHC (MJ/kg) | MARHE (kW/m ²) | TSP (m ²) | <i>t_e</i> (s) | residue (wt %) |
|----------|---------|----------------------------------------|--------------------------|--------------------------|--------------|----------------------------|-----------------------|--------------------------|----------------|
| PIR-DEHP | 48 | 320.6 | 56 | 39.2 | 19.0 | 137 | 7.8 | 1185 | 17 |
| M20-DEHP | 62 | 234.4 | 182 | 72.8 | 19.0 | 153 | 14.1 | 782 | 26 |
| M20 | 72 | 361.1 | 98 | 86.9 | 19.8 | 191 | 15.0 | 930 | 13 |

^aThe highest PHRR is shown.

as shown in Figure 4. First, the PIR-DEHP elastomer was prepared by reacting the PIR-DEHP prepolymer with Lupraphen and 15 wt % BDO in the polyol component in solvent-free conditions. The used PIR-DEHP prepolymer had an NCO content = 18.1 wt %, $M_n = 590$ g/mol, calculated $f_n = 2.5$, and molar ratio of U:A:ISR of 1:0.5:0.8 (Figures S8 and S9).

In order to compare the thermal stability of PIR structures with polymeric MDI regardless of the effects of phosphorus content, the M20-DEHP prepolymer was prepared by reacting M20 with the same amount of DEHP as in the PIR-DEHP prepolymer. After that, the M20-DEHP elastomer was prepared by reacting the M20-DEHP prepolymer with Lupraphen and 15 wt % BDO in the polyol component. Another M20 elastomer was prepared by reacting M20 with Lupraphen and 15 wt % BDO in the polyol component. Both of the elastomers were cast using the same procedure as the PIR-DEHP elastomer in bulk conditions (Table S5 and Figure S10).

The TGA and DMA results of three elastomers are shown in Figure S11. With the same amount of DEHP as well as similar amounts of aromatic content, polyol and BDO, the PIR-DEHP and M20-DEHP elastomers had similar $T_{d5} \approx 265$ °C, char formation $\approx 23\%$, and $T_g \approx 40$ °C. However, without DEHP and PIR, the M20 elastomer showed a lower char formation of only 16%.

The combustion behavior of the PIR-DEHP, M20-DEHP, and M20 elastomers was initially evaluated by cone calorimetry and the time to ignition (TTI, s), peak of the heat release rate (PHRR, kW/m²), time to PHRR (*t_p*, s), total heat release (THR, MJ/m²), average effective heat of combustion (AEHC, MJ/kg), maximum average rate of heat emission (MARHE, kW/m²), total smoke production (TSP, m²), time to

extinguishment (*t_e*), and mass residue (wt %) obtained using a heat flux of 35 kW/m² are shown in Figure 5 and Table 2.

From Figure 5a, it is noted that the HRR curves of all the elastomers show two peaks associated with two-step decomposition, which is also evident from the TGA curves in Figure S11. Typically, the first decomposition step corresponds to the decomposition of urethane bonds in PU and the second step is caused by the decomposition of the soft segment.^{27,29,48} The higher first PHRR peak of the PIR-DEHP elastomer compared to that of the M20-DEHP elastomer may be due to the additional rupture of allophanate bonds. The endothermic decomposition of the PIR structures and the effect of phosphorus content are attributed to a fast decrease of the HRR after reaching the PHRR, leading to a reduction of 55% in THR compared to the M20 elastomer.^{49–51} The decomposition of PIR structures also leads to lower char residue compared to the M20-DEHP elastomer.^{52,53} On the other hand, the M20-DEHP elastomer has the lowest PHRR and shortest combustion time, leading to high char residue, whereas the broad HRR curve results in a higher THR in comparison to the PIR-DEHP elastomer. The same trend was observed in cone calorimetry measurements using a heat flux of 50 kW/m² (Figure S12). In addition, an important factor to show the activity of flame retardants in the gas phase is the EHC, which means the combustion extent of volatiles in the gas phase.^{29,35,54} Despite the differences in the HRR and char residue, the PIR-DEHP and M20-DEHP elastomers have similar average EHCs, which are slightly reduced relative to the M20 elastomer, indicating that the phosphorus content has a minor effect in the gas phase. Finally, the PIR-DEHP elastomer showed the lowest TSP compared to the other two elastomers. As the smoke production is one of the major hazards of fire, lowering the TSP helps improve the fire safety of the material.

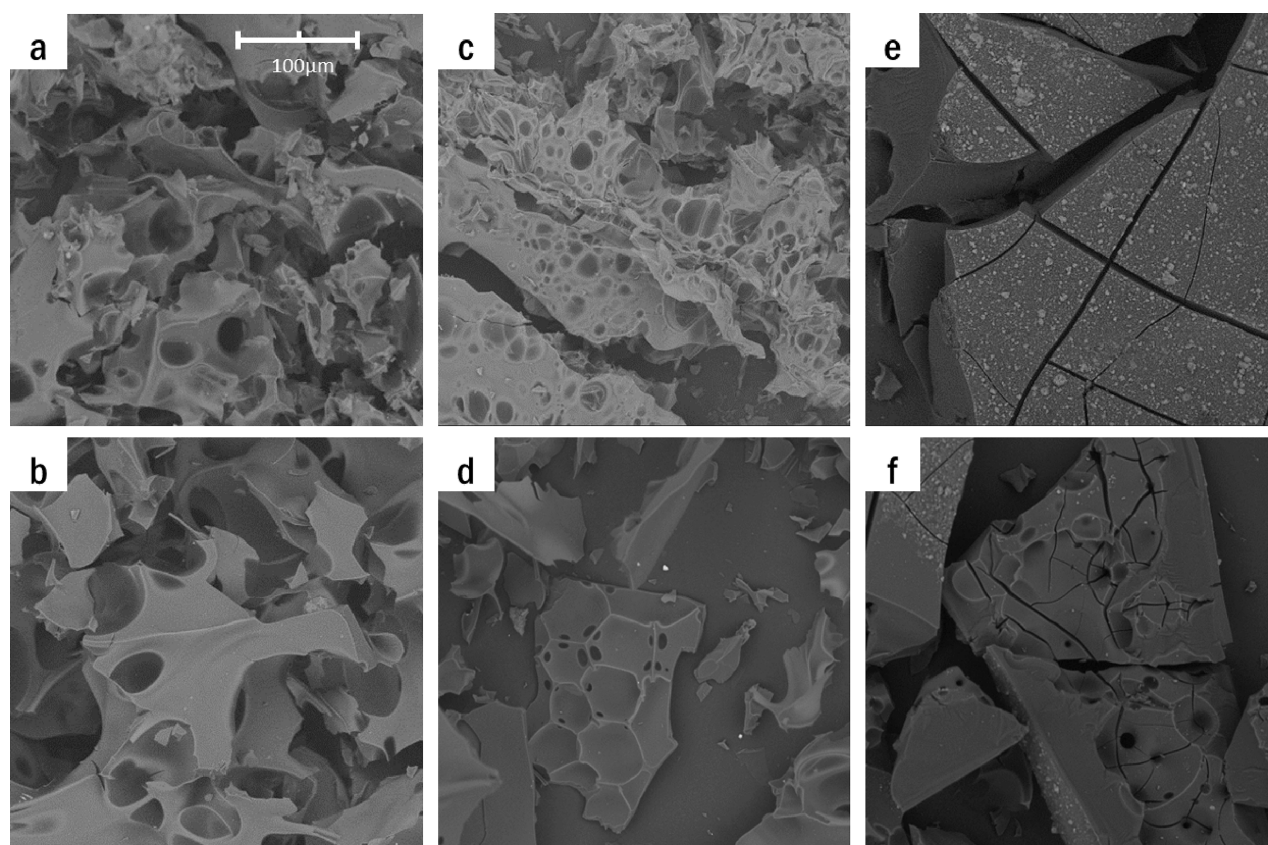


Figure 6. SEM images (100 μm , 780 \times , 10 kV) of elastomer char residues obtained from the (a) PIR-DEHP elastomer surface, (b) PIR-DEHP elastomer interior, (c) M20-DEHP elastomer surface, (d) M20-DEHP elastomer interior, (e) M20 elastomer surface, and (f) M20 elastomer interior.

The PIR structures in combination with the phosphorus content help reduce the TSP during the combustion.

Scanning electron microscopy (SEM) images of the char residues after cone calorimetry measurements are shown in Figure 6. The porous char of both PIR-DEHP and M20-DEHP elastomers might be the result of decomposition of the elastomers and the release of volatiles. It is also notable that the surface and inside char images of the PIR-DEHP elastomer are similar but that they differ a lot for the M20-DEHP elastomer. According to the char residue images (Figure S13), the PIR-DEHP elastomer had no expansion, resulting in a more even morphology of the char residue. However, the expansion of the M20-DEHP elastomer led to a different morphology with a higher concentration of pores on the surface. Although the interior of the elastomer sample cracked to smaller pieces due to expansion, less pores were observed. The M20 elastomer was combusted to a great extent with a lot of ashes and dense char observed.

The char residues of the elastomers were further studied with Raman spectrometry as shown in Figure S14. Two strong overlapping peaks were observed at 1348 and 1586 cm^{-1} , which are attributed to the D band (amorphous structure) and G band (graphitic structure) of C=C bonds, respectively. The integral ratio of the D band to G band is often used as a characteristic parameter for the graphitization degree of the char residues.^{32,55} A lower value of I_D/I_G indicates a higher degree of graphitization that reduces the release of polymer volatiles from the char. After peak deconvolution, the integrals of the D band and G band were obtained and the ratio of I_D/I_G was calculated. The I_D/I_G ratios of PIR-DEHP, M20-DEHP,

and M20 elastomers are 1.90, 2.31, and 1.95, respectively. This indicates that the combination of phosphorus and PIR content in the PIR-DEHP elastomer helps to promote amorphous char into a graphitic structure, leading to low I_D/I_G ratios.

3. CONCLUSIONS

We investigated a synthetic pathway to incorporate PIR and phosphorus motifs (DEHP) in PU elastomers via covalent bonds in order to improve their thermal stability as well as flame retardancy. The PIR-DEHP elastomers are stiff and exhibit a high T_g . Moreover, they show high char formation according to TGA measurements and low THR and TSP according to initial cone calorimetry measurements.

Our current study highlights the preparation of the liquid PIR-DEHP prepolymer with a high concentration of isocyanurate structures via cyclotrimerization of mono- and difunctional isocyanates. The use of a phosphorus-containing alcohol also creates a way to introduce covalently bound phosphorus atoms in PU materials instead of using phosphorus-containing additives. The combination effect of PIR and phosphorus motifs improves the char formation and flame retardancy of the PU materials. This effect should be further studied by additional cone calorimetry measurements according to the industrial norms and fire behavior tests such as UL94, limiting oxygen index (LOI), and gas chromatography–mass spectrometry (GC–MS) measurements.

The liquid PIR-DEHP prepolymer also offers prospects for the use of the PIR-DEHP prepolymer in other industrial applications such as rigid PU foams, compact thermosets, and

coatings where a solvent-free synthesis and flame retardancy are required. By improving the intrinsic flame retardancy of PU materials, the use of conventional flame-retardant additives can be reduced. Moreover, it is expected that the physical properties, thermal stability, and flame retardancy of the PU materials based on PIR prepolymers can be tuned by varying phosphorus compounds.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsapm.3c00223>.

Additional detailed experimental data including: general information (materials, synthesis procedures, and methods), ^1H and ^{13}C NMR spectra of DEHP, kinetic study of the reaction between 4,4'-MDI and monofunctional alcohol, real-time temperature and torque during the synthesis of PIR-DEHP prepolymers, original GPC curves of PIR-DEHP prepolymers, recipes and photos of elastomers, data tables of DMA and TGA measurements, TGA measurement data of classical elastomers, quantitative ^{13}C NMR spectrum and GPC curves of the PIR-DEHP prepolymer for casting cone calorimetry specimens, recipes and photos of the elastomers for cone calorimetry measurement, TGA and DMA measurements of the elastomers for cone calorimetry measurement, HRR and THR curves of elastomers measured by the cone calorimeter under a heat flux of 50 kW/m^2 , photos of the char residue, and Raman spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Rint P. Sijbesma – Department of Chemical Engineering and Chemistry and Institute for Complex Molecular Systems, Eindhoven University of Technology, 5600 MB Eindhoven, Netherlands; orcid.org/0000-0002-8975-636X;
Email: r.p.sijbesma@tue.nl

Željko Tomović – Department of Chemical Engineering and Chemistry and Institute for Complex Molecular Systems, Eindhoven University of Technology, 5600 MB Eindhoven, Netherlands; orcid.org/0000-0002-7944-5728;
Email: z.tomovic@tue.nl

Authors

Yunfei Guo – Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, 5600 MB Eindhoven, Netherlands

Julian Kleemann – BASF Polyurethanes GmbH, 49448 Lemförde, Niedersachsen, Germany

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acsapm.3c00223>

Notes

The authors declare no competing financial interest.

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