Synthesis of phosphorus-containing polyurethanes and poly(urethane-acrylate)s

Mahir Burak SÜDEMEN[1,*], **Hacer Ayşen ÖNEN**[2]

[1]Department of Polymer Science and Technology, Institute of Sciences and Technology,
İstanbul Technical University, İstanbul, Turkey

[2]Department of Chemistry, Faculty of Sciences and Letters, İstanbul Technical University, İstanbul, Turkey

Abstract: Solvent-based polyurethanes and poly(urethane-acrylate)s were synthesized using phosphorus-containing polyester polyols in order to compare the thermal properties of different polymer types. Since the location of the phosphorus group might have vital importance when comparing the thermal properties, phosphorus groups were kept on the pendant chains in poly(urethane-acrylate)s using phosphorus-containing urethane macromonomers while they were kept on the backbone in polyurethanes. The effect of molar mass of polyurethanes and pendant urethane chains of poly(urethane-acrylate)s on thermal properties was also investigated. Characterization of the synthesized polymers was carried out using FT-IR, GPC, NMR, and DSC followed by evaluation of the thermal properties.

Key words: Polyurethane, poly(urethane-acrylate), phosphorus flame retardant

1. Introduction

Research on high performance coating polymers has long been an interest for both the academic and industrial communities. In the last few decades, researchers have systematically created new approaches for coating polymers to meet the requirements of the application areas. One of the coating polymers that has gained importance in the last few decades in the industry is polyurethane. Polyurethane coatings find applications in many industries such as textile, leather, paint, aerospace, and metal coating in an increasing trend due to their advantageous properties such as mechanical durability, chemical resistance, and low temperature curing along with their highly elastomeric properties.[1−5] On the other hand, the main disadvantage of polyurethanes is their high price in the market due to expensive raw materials such as di-isocyanates. In addition to the high cost, the production of polyurethanes is more problematic compared to the other polymerization systems due to the high reactivity of isocyanates with impurities such as water.[6]

Another important polymer type used in the coating industry is acrylic polymer. While the mechanical properties and chemical resistances of acrylic polymers are inferior compared to polyurethanes, their cost efficiency is making them the choice for low cost applications. The ability to tailor the required properties using the wide selection of commercially available acrylic monomers also makes this polymer type useful for coating industries such as paint, garment, furniture, and textile.

The disadvantages of both polyurethane and polyacrylate coatings are somewhat overcome by hybrid coatings. One of the methods for obtaining optimized properties is through physical blending of the polyurethane and polyacrylate.[7] While higher mechanical properties, solvent and chemical resistances, and toughness are

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*Correspondence: sudemen@gmail.com

gained by polyurethanes, lower cost and outdoor resistance are provided by polyacrylates. Although it is a simple and effective way to achieve some of the hybrid properties, physical blending fails to provide the desired properties in performance coatings.[8] Another method researchers focus on is emulsion acrylic polymerization using polyurethane dispersions as the emulsifier.[9−12] In this case, the resulting polymer network generates more durable polymers compared to a simple blending system. However, this system fails to overcome the shortcomings of blending technology. For this reason, research on covalently bonded hybrid systems is recently attracting a lot of attention using urethane and acrylate chemistry. Covalent hybrid systems focus on the polymerization of acrylic terminated urethane macromonomers with acrylic monomers.[13−18] One of the distinct advantages of this method in performance coating development is the ability to combine different monomer types of the two different polymer technologies in order to obtain the desired properties from the coated substrate. In addition to the benefits gained by chemical versatility, the structural differences offered by urethane-acrylate polymers might provide interesting properties compared to linear polyurethanes or polyacrylates. Even though there are a variety of studies on the polymerization of urethane macromonomers with acrylic monomers, there are no reports that compare the final properties of poly(urethane-acrylate)s with those of linear polyurethanes. Therefore, in order to understand the effect of structural differences between linear polyurethanes and poly(urethane-acrylate)s on the final properties of polymers, we designed and synthesized phosphorus-containing polyurethanes and poly(urethane-acrylate)s. Phosphorus is kept on the backbone of polyurethanes and on the pendant urethane macromonomers of poly(urethane-acrylate)s in order to compare the efficiency of pendant chains of poly(urethane-acrylate)s with linear polyurethanes on thermal properties. After the polymerizations, the effect of phosphorus content and molar mass on the thermal properties of poly(urethane-acrylate)s and linear polyurethanes were discussed.

2. Results and discussion
2.1. Synthesis of polyester polyols

Polyester polyols (PEPs) with two different molar masses were synthesized using adipic acid, 1,6-hexanediol, and neopentyl glycol via an esterification reaction as shown in Figure 1. The synthesized polyester polyols were designated as PEP-L and PEP-H, with "L" and "H" indicating low and high molar masses, respectively.
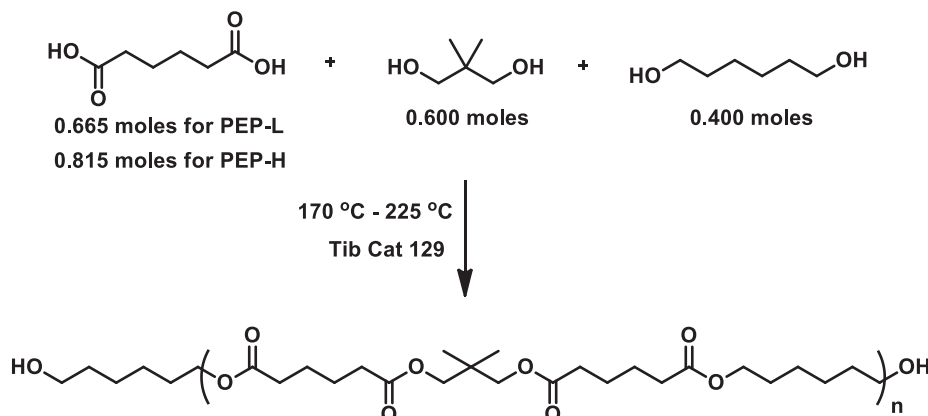

Figure 1. Synthesis of polyester polyols.

FT-IR spectra of the polyester polyols showed major polyester bands at 1729 cm^{-1}, 2866/2936 cm^{-1}, and 1371 cm^{-1} arising from carbonyl stretching vibration, CH$_2$ symmetric and asymmetric stretching vibrations,

and gem-dimethyl stretching vibration of neopentyl glycol, respectively, as shown in Figure 2. The free hydroxyl group appeared as a broad band around 3500 cm^{-1}.
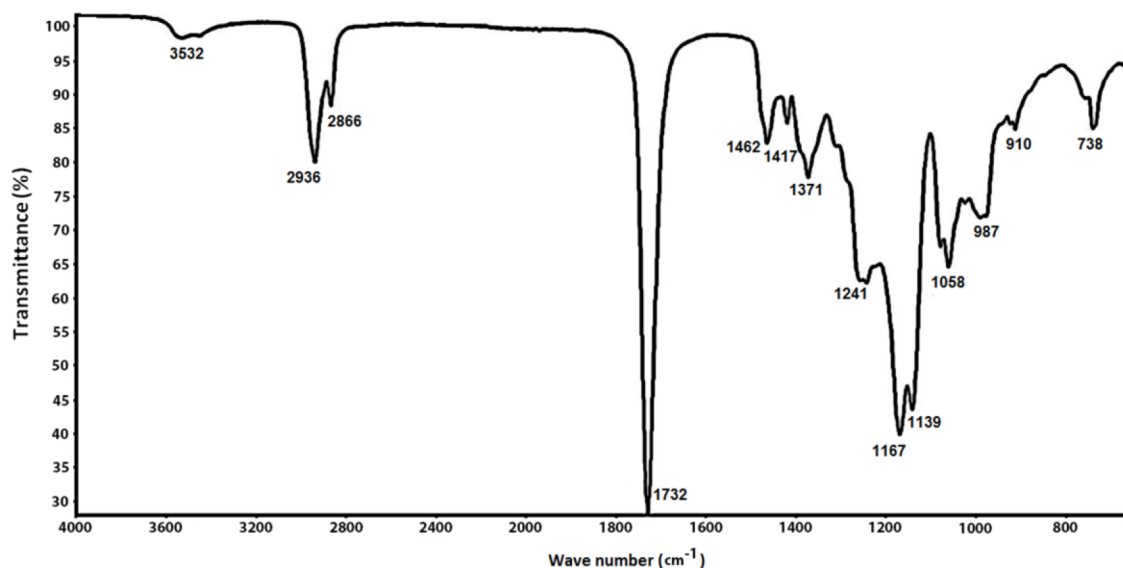

Figure 2. FT-IR spectrum of polyester polyol.

Phosphorus-containing polyester polyols (PPEPs) with varying phosphorus contents were synthesized as shown in Figure 3. In order to adjust the phosphorus contents, the molar ratio of phenyl dichlorophosphate and PEP-L/PEP-H was changed. While two of the PPEPs, PPEP-LP and PPEP-HP, were synthesized using PEP-H to be used in the synthesis of polyurethanes, the other two PPEPs, PPEP-LM and PPEP-HM, were synthesized using PEP-L to be used in the synthesis of macromonomers.
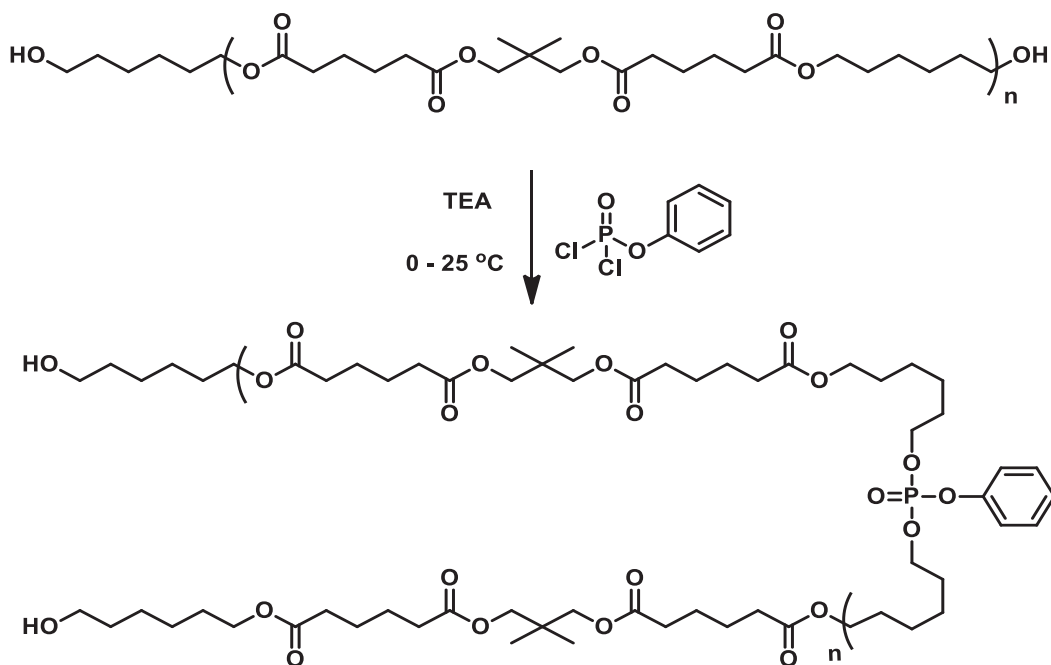

Figure 3. Synthesis of phosphorus-containing polyester polyols.

After the reaction of synthesized polyester polyols with phenyl dichlorophosphate in order to obtain phosphorus-containing polyester polyols, new bands appeared in the FT-IR spectra as shown in Figure 4. Bands at 1593 cm^{-1} and 1491 cm^{-1} were attributed to the stretching vibrations of the phenyl group on the polyester polyol backbone. Bands at 1256 cm^{-1}, 1015 cm^{-1}, and 939 cm^{-1} arose from P=O stretching, P–O–C asymmetric stretching, and P–O–Ph symmetric stretching, respectively. The monosubstituted phenyl ring showed a strong band at 767 cm^{-1}.
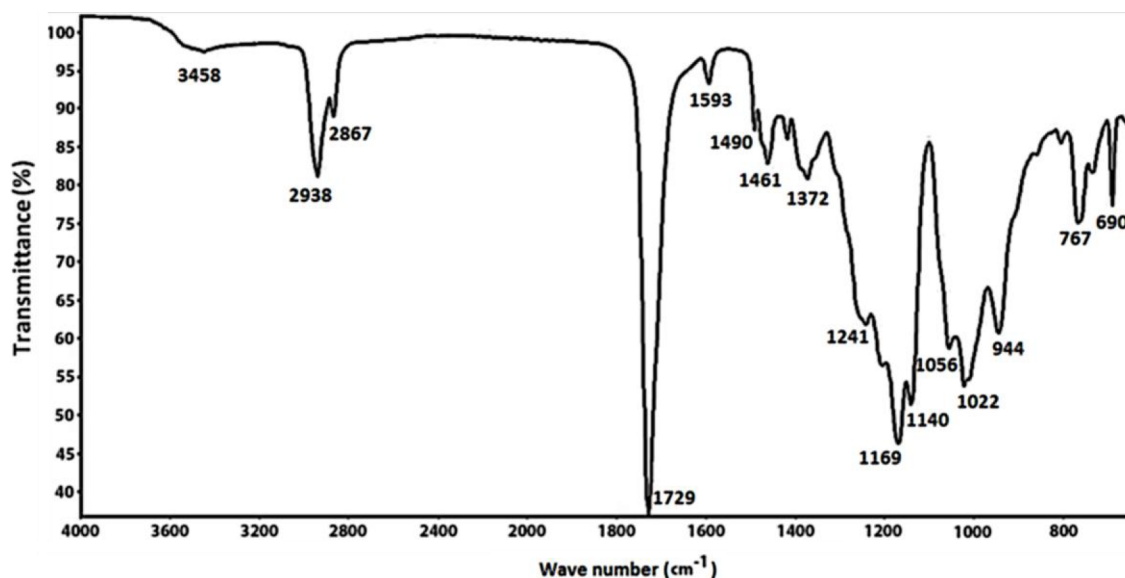

Figure 4. FT-IR spectrum of phosphorus-containing polyester polyol.

DSC studies showed two different transitions for both Tg and Tm of polyester polyols. While Tg values lower than –58 °C appeared as the major transitions, values at higher temperatures showed minor transitions. The two different Tg and Tm values could be due to distribution of the monomers throughout the polyols. While polyol chains containing more 1,6-hexanediol in the backbone will create polyols with higher Tg and Tm values, chains containing more neopentyl glycol will result in lower Tg and Tm values. After the reaction of polyester polyols with phenyl dichlorophosphate, both Tg and Tm values increased as shown in Table 1. Increases in the values in both transitions indicate successful incorporation of phenyl phosphate moiety.

Table 1. Thermal transitions of polyester polyols.

Polyester polyols				
	Tg$_1$	Tg$_2$	Tm$_1$	Tm$_2$
PEP-H	–69.7 °C	–30.8 °C	14.1 °C	26.1 °C
PEP-L	–71.6 °C	–32.4 °C	16.8 °C	25.4 °C
PPEP-LP	–67.0 °C	–26.1 °C	31.2 °C	39.8 °C
PPEP-HP	–65.2 °C	–22.8 °C	32.6 °C	41.4 °C
PPEP-LM	–64.8 °C	–23.4 °C	35.1 °C	41.6 °C
PPEP-HM	–58.1 °C	–18.3 °C	35.3 °C	43.8 °C

2.2. Synthesis of polyurethanes

Synthesized phosphorus-containing polyester polyols were subsequently used in the synthesis of the phosphorus-containing polyurethanes with low and high phosphorus contents (LPC – HPC), which were 0.63%–0.64% and 1.11%–1.12% over dry mass. Polyurethanes were synthesized in two different molar masses for each phosphorus content in order to see the effect of molar mass on char yields. Molar masses were changed by varying the repeating units, which is NCO/OH ratios as shown in Figure 5.
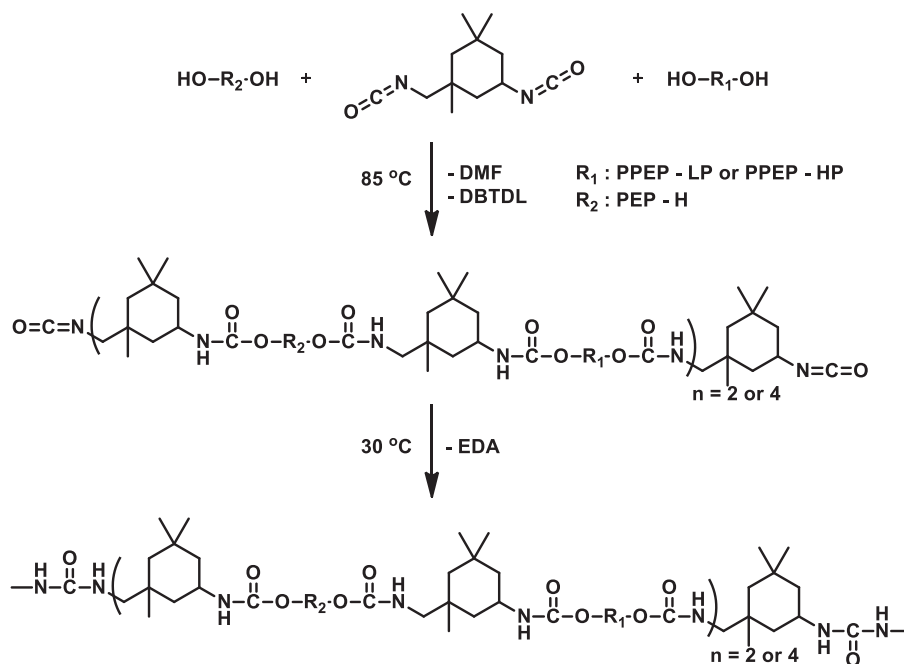

Figure 5. Synthesis of polyurethanes.

In order to adjust the phosphorus contents equally, PEP-H was used along with the respective phosphorus-containing polyester polyols, PPEP-LP and PPEP-HP. While adjusting the phosphorus contents the molar amount of a polyol component was increased the same amount of another polyol component was decreased and NCO/OH ratio was kept constant. All of the differentiations of phosphorus-containing polyurethanes are summarized in Figure 6.
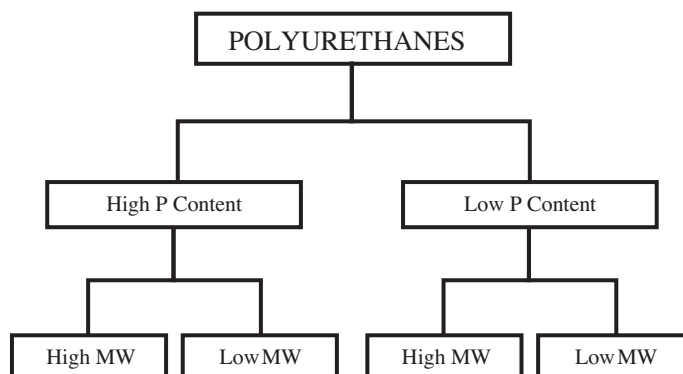

Figure 6. Schematic representation of phosphorus different polyurethanes.

Dried films of polyurethanes in FT-IR exhibited the characteristic absorption bands of stretching vibration of urethane –NH and stretching vibration of urethane carbonyl group at 3380 cm^{-1} and 1729 cm^{-1}, respectively. In addition, the bands that appeared at 1530 cm^{-1} and 1380 cm^{-1} were attributed to NH bending and C–N stretching vibrations in the spectra. Urea carbonyl at 1663 cm^{-1}, which is created by chain extension with ethylenediamine, was also observed. The spectra also showed the presence of CH asymmetric and symmetric stretching vibrations at 2960 cm^{-1} and 2898 cm^{-1}. Bands related to the aromatic ring were observed only as small peaks at 1591 cm^{-1} and 1491 cm^{-1}. However, none of the bands related to the phosphorus atom were identifiable since they were overrun by other bands of the polymer.

DSC measurements of PUs showed one Tg and two Tm transitions. Tg transition values, which are a direct result of polyol soft segmental motion, were between –40 °C and –60 °C while the Tm transition values, which were also observed in phosphorus-containing polyester polyols, were 1–16 °C for Tm_1 and 35–40 °C for Tm_2 as shown in Table 2. Two different polyurethane DSC plots are displayed in Figure 7.

Table 2. Thermal transitions of polyurethanes.

Phosphorus-containing polyurethanes							
HPC	Tg_1	Tm_1	Tm_2	LPC	Tg_1	Tm_1	Tm_2
LMW	–50.5 °C	15.7 °C	32.6 °C	LMW	–49.6 °C	1.1 °C	39.1 °C
HMW	–51.6 °C	13.4 °C	33.9 °C	HMW	–50.2 °C	15.7 °C	35.9 °C

The ^{1}H NMR spectra of polyurethanes exhibited $–CH_2$ and $–CH_3$ polyester soft segment bands originating from AA, 1,6-HDO, and NPG between 0.8 ppm and 4.2 ppm. The peaks attributed to –CH, $–CH_2$ and $–CH_3$ IPDI skeleton peaks were between 0.9 ppm and 3.8 ppm mostly coinciding with polyester peaks. The peaks appearing between 7.1 ppm and 7.4 ppm were assigned to the phenyl ring of PPEP soft segment. Urethane and urea –NH protons were found at 7.0 ppm and 8.0 ppm respectively as shown in Figure 8.

2.3. Synthesis of macromonomers

In order to synthesize poly(urethane-acrylate)s, four phosphorus-containing macromonomers were first synthesized with two different repeating units as shown in Figure 9.

Macromonomers were synthesized by first creating an NCO terminated urethane oligomer and end capping the remaining NCO groups using an acrylic moiety such as hydroxyethyl acrylate (HEA) and a reactive small group such as n-butanol. This method has certain drawbacks. The major drawback is the formation of unreactive urethane oligomers in the macromonomer mixture as shown in Figure 10. Generally, a decrease in the amount of HEA causes an increase in the amount of unreactive butanol terminated oligomers. On the other hand, an increase in the HEA amount to decrease/eliminate the unreactive oligomers causes an increase in the concentration of macromonomers with HEA at both ends, which will act as a cross-linker during radical polymerization. As unreactive oligomers lower the material quality in the final polymer, end-capping was carried out with a mole ratio of 60%/40% HEA/n-butanol in order to decrease the amount of unreactive oligomers.

The phosphorus contents of macromonomers were adjusted in such a way that after the polymerization with an acrylic monomer (35/65 w/w) the phosphorus contents of the poly(urethane-acrylate)s would be in the range of 0.63%–0.64% and 1.11%–1.12% over dry mass for LPC and HPC poly(urethane-acrylate)s, respectively.

Dried films of macromonomers in FT-IR showed bands similar to those of polyurethanes. The spectra exhibited the presence of urethane N–H groups at around 3380 cm^{-1}, CH asymmetric and symmetric stretching vibrations at 2870 cm^{-1} and 2960 cm^{-1}, a urethane carbonyl group at 1729 cm^{-1}, a C=C double bond at
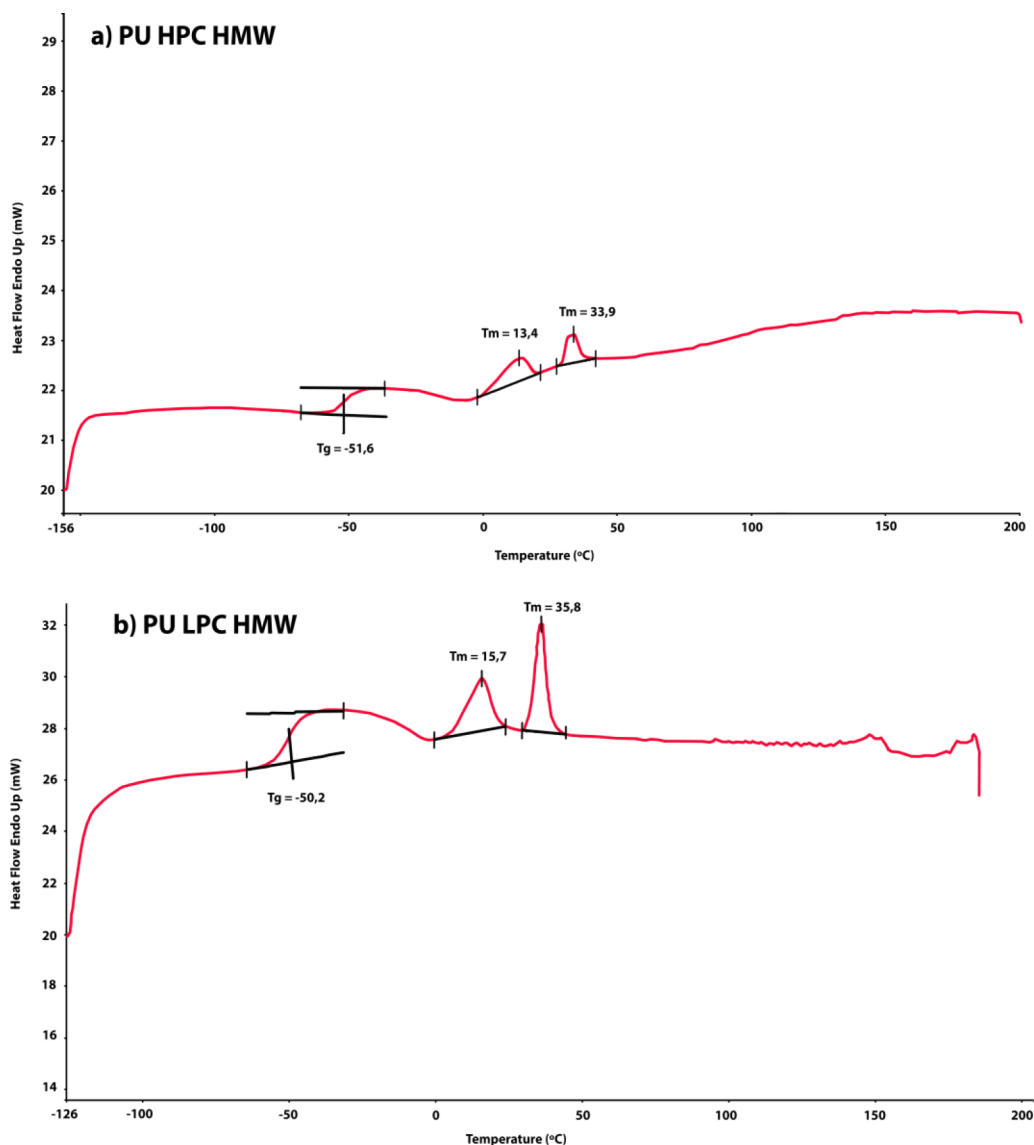
Figure 7. DSC plots of polyurethanes. a) PU HPC HMW, b) PU LPC HMW.

1650 cm^{-1}, and N–H bending and C–N stretching vibrations at 1535 cm^{-1} and 1371 cm^{-1}, respectively. The low intensity bands at 1593 cm^{-1} and 1490 cm^{-1} were attributed to the aromatic ring in the structure. NMR spectra of urethane macromonomers were also similar to polyurethane spectra with soft segment aliphatic peaks and IPDI skeleton peaks between 0.8 ppm and 4.2 ppm as shown in Figure 11. In addition to the phenyl ring peaks between 7.1 ppm and 7.4 ppm, the spectra also displayed the urethane proton at 6.9 ppm and double bond protons of the α,β-unsaturated system that belongs to HEA moiety between 5.8 ppm and 6.5 ppm. Unlike the polyurethane spectra, there were no urea protons in the macromonomer ^{1}H NMR spectra since no amine chain extender was used in the synthesis of urethane macromonomers.

2.4. Synthesis of poly(urethane-acrylate)s

Before starting the radical polymerization of phosphorus-containing urethane macromonomers with an acrylic monomer, the optimum amount of initiator was determined. The concentration of the initiator was varied from
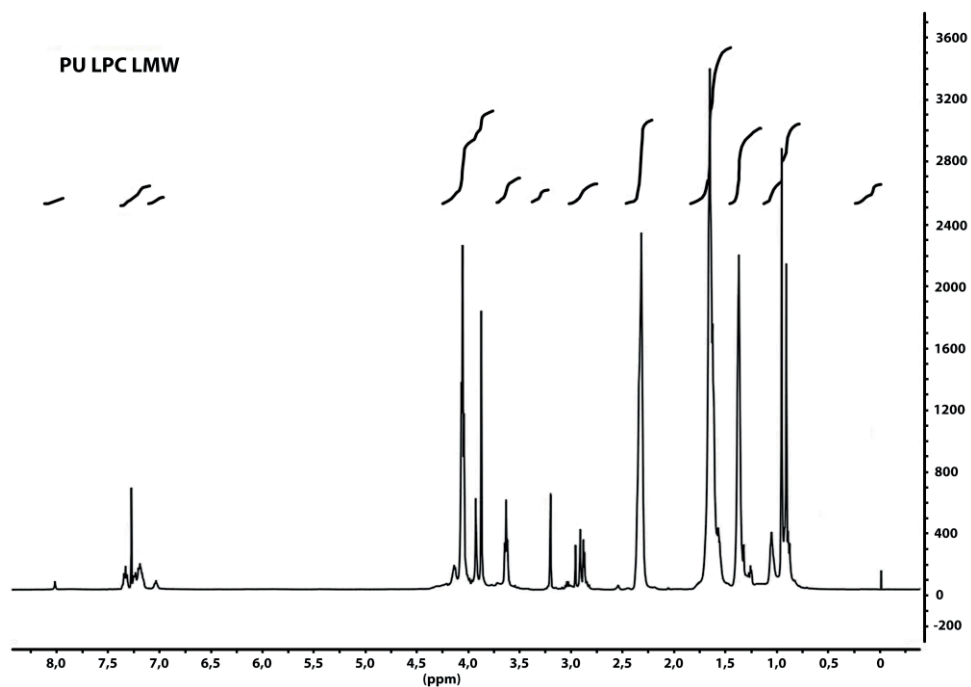
Figure 8. ^{1}H NMR spectrum of LPC, LMW polyurethane.
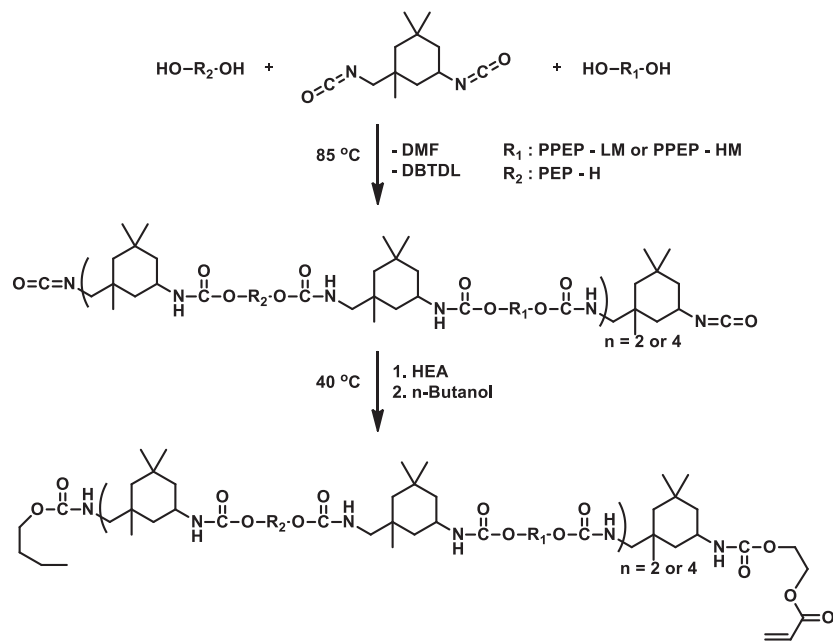
Figure 9. Synthesis of macromonomers.

0.50% to 1.25% (weight over total solids) with 0.25% increments for the polymerization of methyl methacrylate with LPC/LMW macromonomer.

It was observed from GPC measurements that as the amount of initiator was increased the amount of unreacted macromonomer remaining at the end of polymerization decreased as shown in Figure 12. However, using an initiator amount of 1.25% resulted in a high viscosity polymer solution with considerable amounts of

R₁ : Polyol
R₂ : IPDI

1. HEA
2. n-Butanol
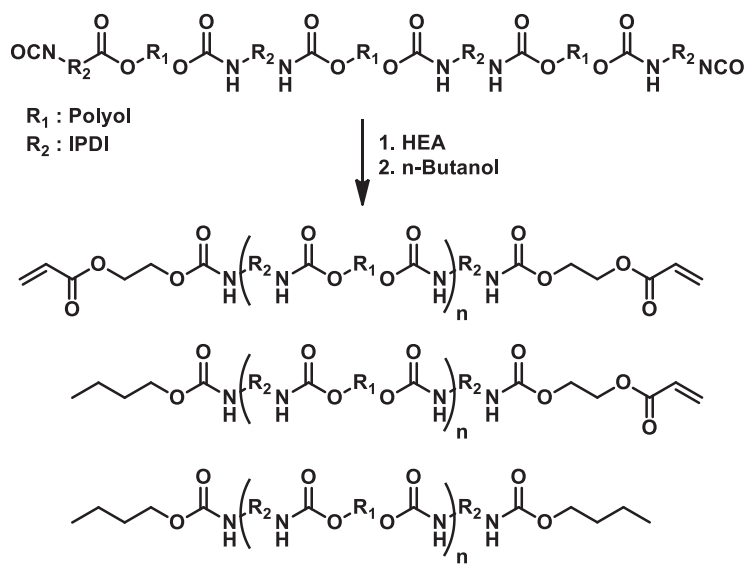
Figure 10. Reactive and unreactive oligomers.
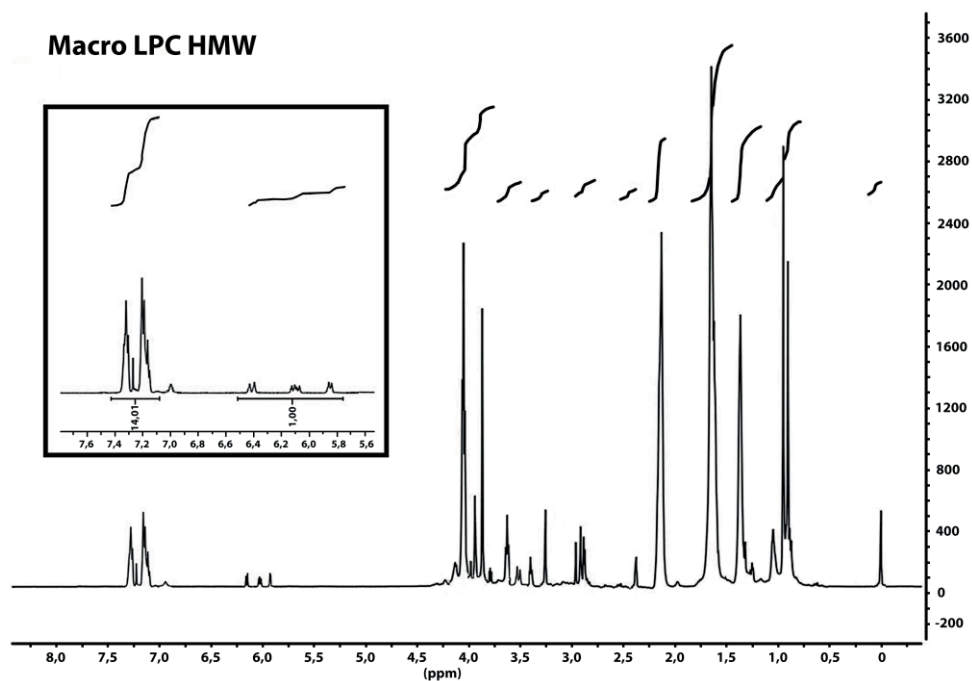
Figure 11. ^{1}H NMR spectrum of LPC, HMW urethane macromonomer.

gel inside the reactor. Therefore, the initiator amount was determined to be 1.0% for the rest of the radical polymerizations.

The synthesized macromonomers were polymerized with MMA (35/65 w/w) in order to obtain poly(urethane-acrylate)s in different phosphorus contents and molar masses as shown in Figure 13. FT-IR spectra of the dried polymer films showed the stretching vibration of N–H groups at around 3405 cm^{-1} as a broad band along with the characteristic peaks of C–H asymmetric and symmetric stretching vibrations at 2961 cm^{-1} and 2898
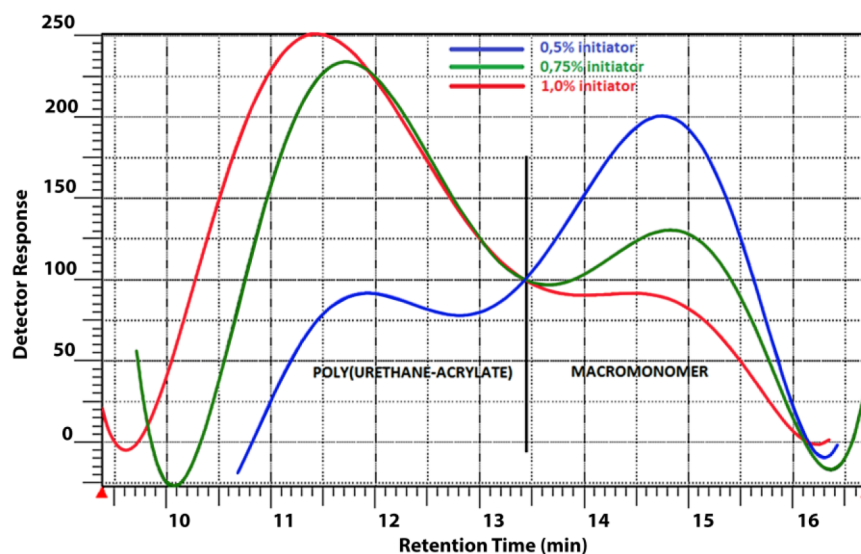
Figure 12. Initiator concentration vs. remaining macromonomer via GPC.

cm^{-1}. Moreover, the spectra displayed the presence of an acrylic/urethane carbonyl group at 1723 cm^{-1}, amide stretching vibration at 1648 cm^{-1}, C–H bending vibrations of acrylic groups at 1448 cm^{-1} and 1385 cm^{-1}, and C–O and C–(C=O)–O stretching vibrations at 1239 cm^{-1} and 1145 cm^{-1}, respectively. The aromatic ring also showed small intensity at 1593 cm^{-1}.
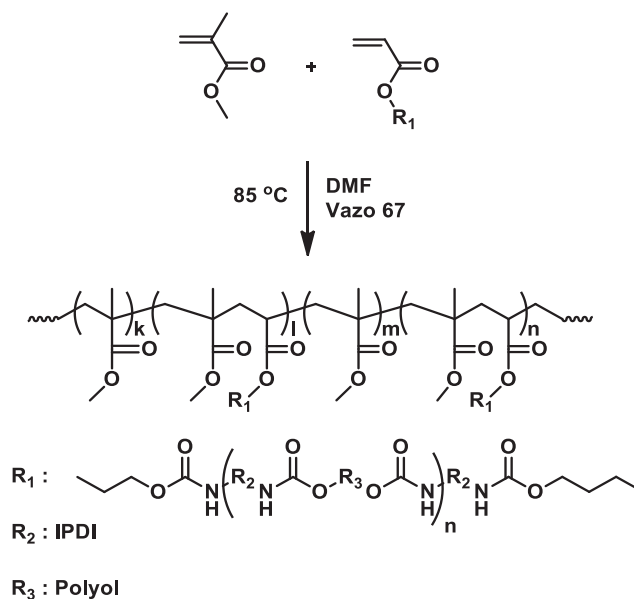
Figure 13. Synthesis of poly(urethane-acrylate)s.

In the DSC measurements of PUAs, multiple glass transitions ranging from –53 °C to 100 °C were observed in the polymers as presented in Table 3. The multiple glass transition values were due to the presence of various polymeric structures and possible crosslinking within the polymer matrix. Due to phase separation of urethane and acrylate parts, Tg values observed below –40 °C were characterized as the soft segmental

motion of urethane pendant groups and Tg values observed above 85 °C were attributed to the polyMMA. The rest of the Tg values resulted from the phase mixing of urethane and acrylate moieties due to the covalent bond between them. Apart from the phase behavior of the polymers, the plasticizing effect of unreactive and unreacted macromonomers played a role in the variety of Tg values as well. Some of the major Tg values are shown for two different poly(urethane-acrylate)s in Figure 14.

Table 3. Thermal transitions of the poly(urethane-acrylate)s.

Phosphorus-containing poly(urethane-acrylate)s					
HPC	Tg_1	Tg_2	Tg_3	Tg_4	Tg_5
LMW	–53.4 °C	–7.6 °C	17.3 °C	87.8 °C	100.7 °C
HMW	–56.4 °C	43.8 °C	89.4 °C	X	X
LPC	Tg_1	Tg_2	Tg_3	Tg_4	Tg_5
LMW	–45.2 °C	1.1 °C	75.6 °C	X	X
HMW	–64.7 °C	–2.1 °C	58.1 °C	89.8 °C	X

The ^{1}H NMR spectra of poly(urethane-acrylate)s exhibited a chemical shift at 3.6 ppm as a singlet due to the methoxy group (O–CH_3) of methyl methacrylate. Moreover, the peaks between 0.8 ppm and 4.2 ppm were attributed to the characteristic IPDI and polyester polyol peaks of urethane macromonomer as shown in Figure 15. In the case of LMW PUAs, the ^{1}H NMR spectra showed the complete disappearance of double bond peaks between 5.8 ppm and 6.5 ppm proving that the macromonomer and monomer were consumed. However, in the case of HMW PUAs, the existence of double bond peaks with low intensities was observed. While increasing the initiator amount would consume all the macromonomers, it would cause deviation from the standard comparison study.

The thermal stabilities of PUs and PUAs were investigated using TGA and char yields were determined as shown in Table 4 and Figures 16 and 17. Char yield is an easy and important test that usually correlates with the material's ability to suppress combustion. Therefore, char yields obtained from the TGA analysis were used to measure the polymer's anticipated fire resistance.

Table 4. Char yields of polyurethanes and poly(urethane-acrylate)s.

Polyurethanes	Char yield %	Poly(urethane-acrylate)s	Char yield %
PU-HPC/LMW	2.120	UrAc-HPC/LMW	1.858
PU-HPC/HMW	1.984	UrAc-HPC/HMW	1.550
PU-LPC/LMW	1.432	UrAc-LPC/LMW	1.347
PU-LPC/HMW	1.578	UrAc-LPC/HMW	1.200

It is generally accepted that urethane linkages are less stable compared to other bonds in polyurethanes due to their easier formation. Therefore, it may be expected that the higher isocyanate-containing polyurethane will show higher weight loss at certain temperature. However, the secondary interactions such as hydrogen bonding and polar–polar interactions restrict the segmental motion and play an important role in increasing the thermal stability of polyurethanes. Therefore, comparison should be carried out only with similar structures.

Within the TGA measurement results of polyurethanes, LMW polyurethanes lost 25% of their weight at lower temperatures compared to their HMW counterparts due to higher urethane linkage content in their structure for both LPC and HPC polyurethanes. Degradation rates of the polyurethanes were close to each other at 50% and 75% weight loss, which took place at 392–408 °C and 412–425 °C, respectively, regardless of
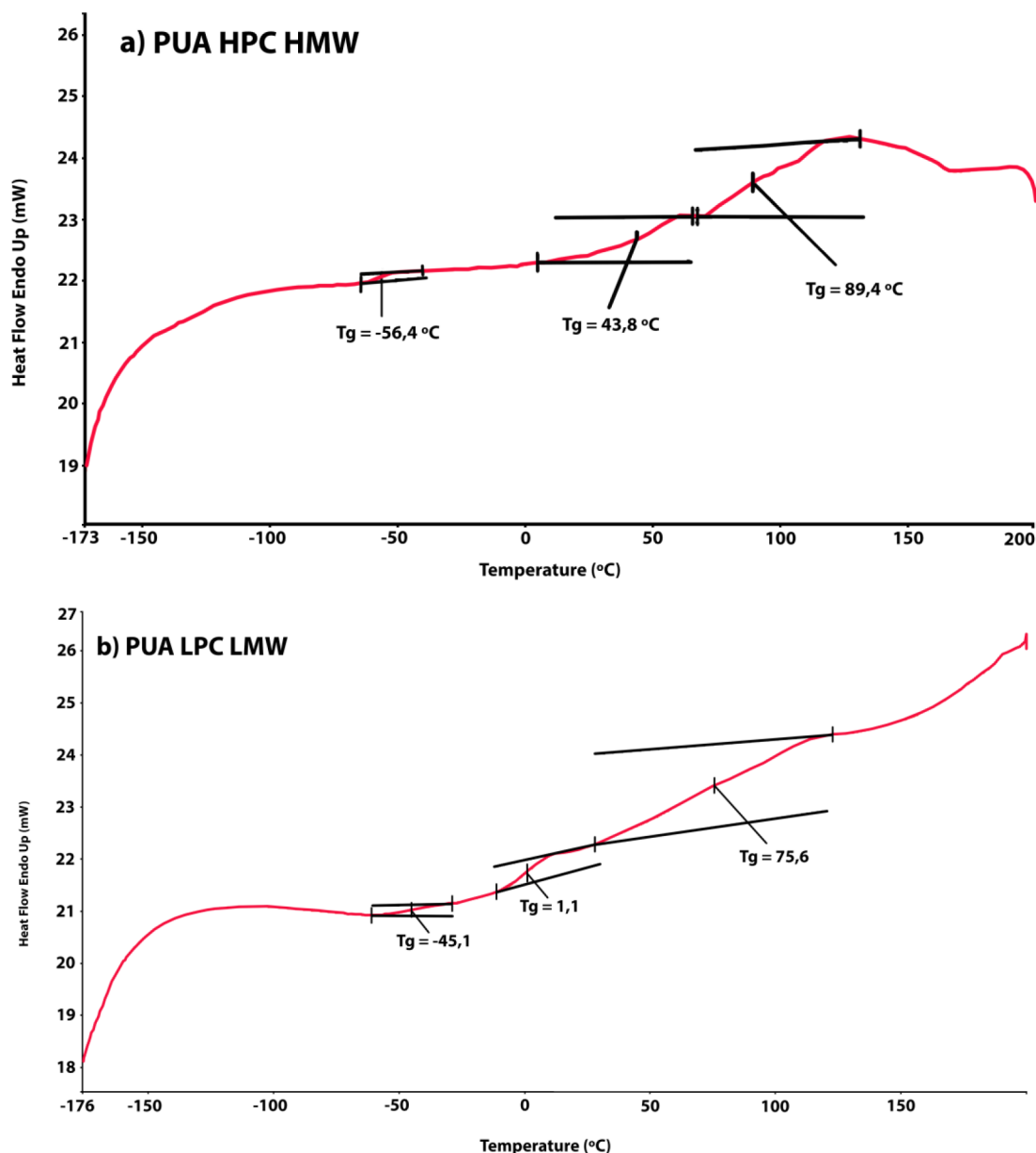
Figure 14. DSC plots of poly(urethane-acrylate)s, a) PUA HPC HMW, b) PUA LPC LMW.

the molar mass. On the other hand, char yields of the polyurethanes showed no conclusive data regarding the effect of molar mass on the fire resistance of polyurethanes. As expected, polyurethanes with higher phosphorus content showed higher char yields.

One of the main differences observed between the TGA results of poly(urethane-acrylate)s and polyurethanes was the temperature at which 25% weight loss took place. While polyurethanes showed 25% weight loss between 361 and 372 °C, poly(urethane-acrylate)s lost 25% of their weight at lower temperature between 316 and 328 °C. Such behavior is mostly due to the incorporated ester linkages arising from MMA. The presence of unreacted and unreactive macromonomers also might have a role in losing 25% weight at low temperature as they are more susceptible to degradation due to their lower molar mass. Moreover, due to their mobility within the matrix,

PUA HPC HMW
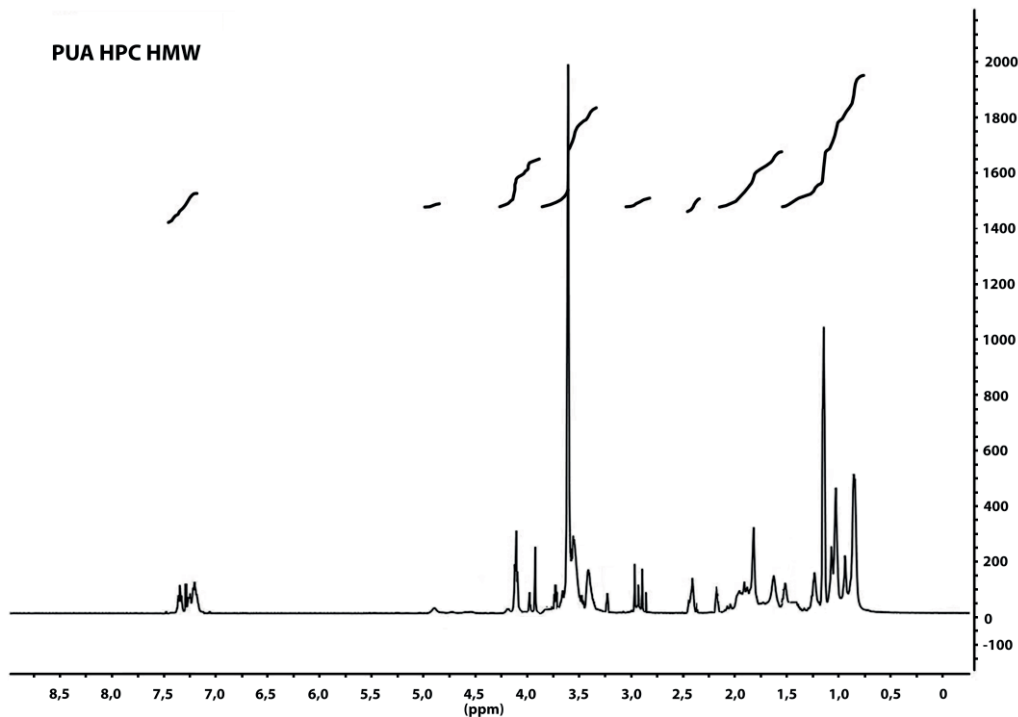
Figure 15. ^{1}H NMR spectrum of HPC, LMW poly(urethane-acrylate).
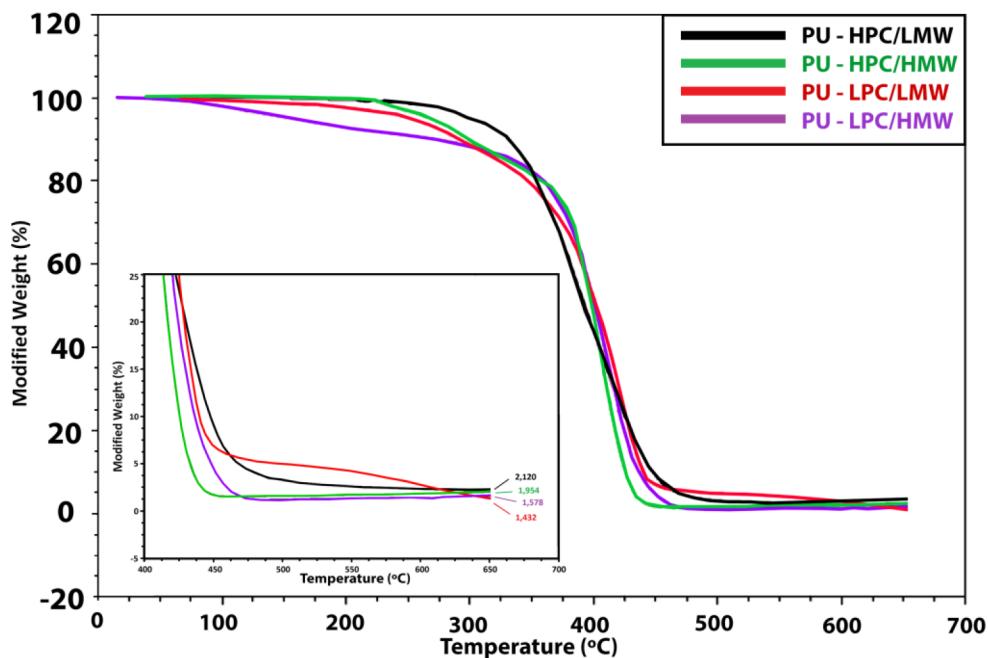
Figure 16. TGA measurements of polyurethanes.

their diffusion towards the surface of the film will be easy and this will result in loss of weight at lower temperature. As the temperature increased, weight loss ratios of polyurethanes and poly(urethane-acrylate)s got closer at 50% weight loss, which took place between 392 and 401 °C for polyurethanes and between 375 and 392 °C for poly(urethane-acrylate)s. The weight loss ratios almost equilibrated and showed 75% weight loss at similar
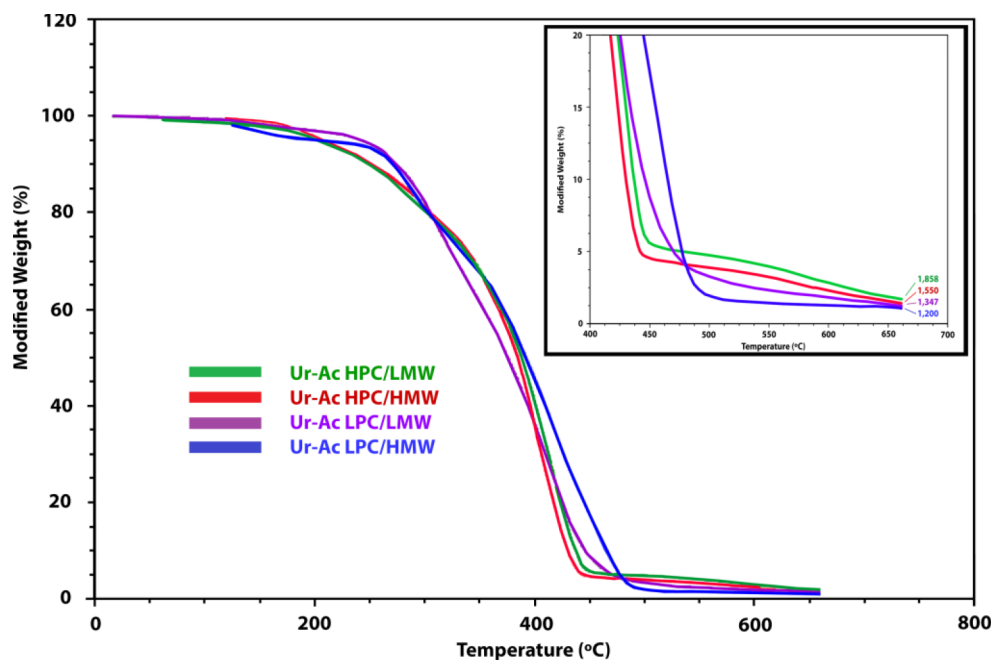
Figure 17. TGA measurements of poly(urethane-acrylate)s.

temperatures between 413 and 424 °C and 411 and 435 °C for polyurethanes and poly(urethane-acrylate)s, respectively. In terms of molar mass, poly(urethane-acrylate)s showed the same behavior as polyurethanes and 25% weight loss was observed at lower temperature for LMW series compared to HMW series due to the higher urethane linkage content of LMW macromonomers. However, TGA results showed that LMW series have more char yield compared to HMW series. This behavior could be due to a lower conversion ratio in the polymerization of HMW macromonomers and MMA as observed in ^{1}H NMR spectra. The presence of unreacted macromonomers plays an important role in diminishing the thermal properties of poly(urethane-acrylate)s along with the other properties of the polymer. Char yields of poly(urethane-acrylate)s were increased after increasing the phosphorus content.

In this study, we endeavored to investigate, understand, and compare the risk of combustion of polyurethanes and poly(urethane-acrylate)s with the same chemical structures on polyurethane backbone and poly(urethane-acrylate) pendant groups. Four different phosphorus-containing polyester polyols were synthesized to obtain phosphorus-containing polyurethanes and urethane macromonomers with varying phosphorus contents and molar masses. Phosphorus-containing urethane macromonomers were further polymerized with MMA to obtain poly(urethane-acrylate)s. All of the synthesized polymers were successfully characterized using end group analysis, FT-IR, NMR, and DSC, and the behavior of polyurethanes and poly(urethane-acrylate)s in thermogravimetric analysis was investigated. This investigation showed that increasing the molar mass of polyurethanes did not have a significant effect on char yields, while increasing the molar mass of pendant groups on poly(urethane-acrylate)s decreased the char yields due to higher content of unreacted macromonomers compared to their low molar mass counterparts as interpreted from NMR. The results obtained from TGA measurements also showed that poly(urethane-acrylate)s started degradation at lower temperature due to unreacted/unreactive oligomers. Information gathered throughout the research revealed that improved polymerization parameters can provide much better results for thermal properties of poly(urethane-acrylate)s. In the case of such achieve-

ment poly(urethane-acrylate)s can close up the performance gap between polyurethanes and polyacrylates with optimized cost.

3. Experimental

3.1. Materials

Isophoronediisocyanate (IPDI) was provided by Evonik A.G., adipic acid (AA) and neopentyl glycol (NPG) were procured from a local dealer, 1,6-hexanediol (HDO) was provided by Perstorp, Tib Cat 129 (Stannous Octoate) and Tib Cat 218 (Dibutyl tin dilaurate) were supplied by TIB Chemicals, VAZO 67 was supplied by DuPont, methyl methacrylate (MMA) and hydroxyethyl acrylate (HEA) were provided by BASF, and triethylamine (TEA), ethylene diamine (EDA), n-butanol, phenyldichloro phosphate (PDCP), THF, CH_2Cl_2, and DMF were obtained from Sigma Aldrich. TEA, THF, and DMF were dried over 4-Å sieves before use. The rest of the chemicals were used as received.

3.2. Equipment

Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer FT-IR Spectrum 100 spectrometer with ATR sampling accessory operating in the range of 4000–500 cm^{-1}. Sixteen scans were averaged for each sample on completely dried films. ^{1}H NMR analysis was performed with a Bruker 400 MHz NMR spectrometer with tetramethylsilane (TMS) as internal standard and deuterated dimethyl sulfoxide (DMSO-d$_6$) used as solvent. DSC analysis was carried out on a PerkinElmer DSC 6000 at working temperature between –170 and 200 °C, heating with a rate of 20 °C/min under nitrogen atmosphere. Thermogravimetric analysis (TGA) of the polymer films was performed using a Q50 TGA analyzer from TA Instruments. Samples were run up to 650 °C with a heating ramp rate of 20 °C/min under N$_2$ atmosphere using samples between 6 and 10 mg.

3.3. Synthesis of polyester polyols

Required amounts of monomers were added to a 1-L 5-necked reaction vessel equipped with a mechanical stirrer, nitrogen inlet, temperature inlet, and Dean–Stark apparatus connected to a condenser. Temperature of the reactor was increased to 150 °C under nitrogen atmosphere and 0.05% (w/w over monomers) Tib Cat 129 catalyst was added. Temperature was increased to 170 °C and kept there until an acid value of 20 mg/KOH was obtained. Once the target acid value was reached, the temperature was increased to 180 °C and then the reaction temperature was increased 15 °C for every 5 mg/KOH decrease in acid value until an acid value below 3 mg/KOH was obtained. The molar ratios of the reactant and specifications of the obtained polyester polyols are shown in Table 5.

Table 5. The molar ratios and specifications of the PEPs.

	PEP-L	PEP-H
Adipic acid	0.665 moles	0.815 moles
1,6-Hexanediol	0.400 moles	0.400 moles
Neopentylglycol	0.600 moles	0.600 moles
Hydroxyl value (mg/KOH)	196.5	104.0
Acid value (mg/KOH)	1.8	2.3
Molar mass	571 g/mol	1078 g/mol

3.4. Synthesis of phosphorus-containing polyester polyols

The required amount of PDCP was dissolved in dry THF (1:3 w_{PDCP}/w_{THF}) and poured into a dropping funnel. In the meantime, TEA and PEP were dissolved in dry THF (1:2 $w_{TEA+PEP}/w_{THF}$) in a 5-necked reaction vessel equipped with a nitrogen inlet, condenser, dropping funnel, temperature inlet, and mechanical stirrer. The solution of PDCP in THF was added dropwise over 1 h to the above-mentioned reactor between 0 and 10 °C and stirred at this temperature for 6 h and overnight at room temperature under nitrogen. After the reaction was terminated, by-product triethylamine hydrochloride salt was filtered and THF was evaporated. The remaining crude product was dissolved in CH_2Cl_2 and the solution was washed with 0.1 M HCl solution to remove the remaining TEA and washed with sodium bicarbonate to remove the remaining HCl. After washing with deionized water and drying over $MgSO_4$, the solvent was evaporated to obtain phosphorus-containing polyester polyol. The molar ratios of the reactants and specifications of the obtained phosphorus-containing polyester polyols are shown in Table 6.

Table 6. The molar ratios of the reactants and specifications of the PPEPs.

	For polyurethane synthesis		For macromonomer synthesis	
	PPEP-LP	PPEP-HP	PPEP-LM	PPEP-HM
PEP-H	2 moles	1.2 moles	-	-
PEP-L	-	-	1.6 moles	1.1 moles
PDCP	1 mole	1 mole	1 mole	1 mole
TEA	2.2 moles	2.2 moles	2.2 moles	2.2 moles
Yield[1]	78%	76%	73%	71%
Hydroxyl value (mg/KOH)	51.4	20.9	43.9	22.9
Acid value (mg/KOH)	3.4	4.1	3.7	4.2
Molar mass	2184 g/mol	5376 g/mol	2554 g/mol	4888 g/mol
P content[2]	1.35%	2.16%	2.76%	4.04%

[1]After extraction procedure. [2]Theoretical values based on reactant moles.

3.5. Synthesis of phosphorus-containing polyurethanes

Polyurethanes were synthesized in a 5-necked 500-mL reaction vessel equipped with a nitrogen inlet, condenser, temperature inlet, and mechanical stirrer. Dry DMF was used in the entire polyurethane synthesis. To the reaction vessel were added the hydroxyl functional reactants specified in Table 7 along with 200 mL of dry DMF. After the reactants were dissolved, a specified amount of IPDI was added along with 5 drops of Tib Cat 218. The flask was heated to 85 °C and stirred until the NCO peak on FT-IR did not change anymore and n-dibutylamine back-titration gave the same result in two consecutive analyses within 1 h. The reaction was cooled to 30 °C and EDA was added for chain extension. The reaction was stirred overnight to complete the reaction between free NCO groups and amine groups of EDA and monitored with FT-IR since measurement of NCO at that level is not reliable via n-dibutylamine back-titration.

3.6. Synthesis of macromonomers

Macromonomers were synthesized in a 5-necked 500-mL reaction vessel equipped with a nitrogen inlet, condenser, temperature inlet, and mechanical stirrer. Dry DMF was used in the entire macromonomer synthesis. To the reaction vessel were added the hydroxyl functional reactants specified in Table 8 along with 200 mL of dry DMF. After the reactants were dissolved, a specified amount of IPDI was added along with 5 drops of

Table 7. Reactant amounts of phosphorus-containing polyurethanes.

Phosphorus-containing polyurethanes				
	HPC PU		LPC PU	
	LMW (g)	HMW (g)	LMW (g)	HMW (g)
IPDI	12.040	11.062	15.598	14.329
PEP-H	36.472	37.448	37.445	38.683
PPEP-HP	51.488	51.490	X	X
PPEP-LP	X	X	46.957	46.988
DMF	200	200	200	200
EDA	0.651	0.332	0.843	0.430
P content[1]	1.112%	1.112%	0.634%	0.634%

[1]Theoretical values based on reactant moles.

Table 8. Reactant amounts of phosphorus containing macromonomers.

Phosphorus-containing macromonomers				
	HPC MM		LPC MM	
	LMW (g)	HMW (g)	LMW (g)	HMW (g)
IPDI	7.616	7.144	12.211	11.440
PEP-H	12.213	13.500	19.581	21.619
PPEP-HM	78.811	78.647	X	X
PPEP-LM	X	X	66.025	65.805
HEA	0.955	0.498	1.531	0.797
n-Butanol	0.406	0.212	0.651	0.339
DMF	200	200	200	200

Table 9. Reactants of phosphorus-containing poly(urethane-acrylate)s.

Phosphorus-containing poly(urethane-acrylate)s				
	HPC PUA		LPC PUA	
	LMW (g)	HMW (g)	LMW (g)	HMW (g)
Macromonomer	105	105	105	105
Vazo 67	1	1	1	1
MMA	65	65	65	65
DMF	165	165	165	165
P content[1]	1.114%	1.112%	0.638%	0.636%

[1]Theoretical values based on reactant moles.

Tib Cat 218. The flask was heated to 85 °C and stirred until the NCO peak on FT-IR remained constant and n-dibutylamine back-titration gave the same result in two consecutive analyses within 1 h. The time for macromonomers to reach a steady NCO level was 5–7 h. Then the reaction was cooled to 40 °C, HEA was added, and the reaction mixture was stirred overnight followed by the addition of an excess amount of n-butanol to clear out the remaining NCO groups and disappearance of the NCO peak on FT-IR was monitored.

3.7. Synthesis of poly(urethane-acrylate)s

Poly(urethane-acrylate)s were synthesized in a 4-necked 500-mL round bottom flask equipped with a mechanical stirrer, thermometer, and nitrogen inlet. A specific amount of urethane macromonomer solution and DMF were added to the reactor as mentioned in Table 9. Once the reaction flask was heated to 85 °C, MMA and initiator (Vazo 67) dissolved in DMF and in separate vessels were added into the reaction flask within 100 and 120 min,

respectively, using a peristaltic pump (Reglo ICC). After the addition was completed, the reaction was kept stirring for another 20 h at 85 °C.

Acknowledgment

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