Supporting information for

Synthesis of polyisocyanurate prepolymer and the resulting flexible elastomers with tunable mechanical properties

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1. Synthesis of PIR prepolymer

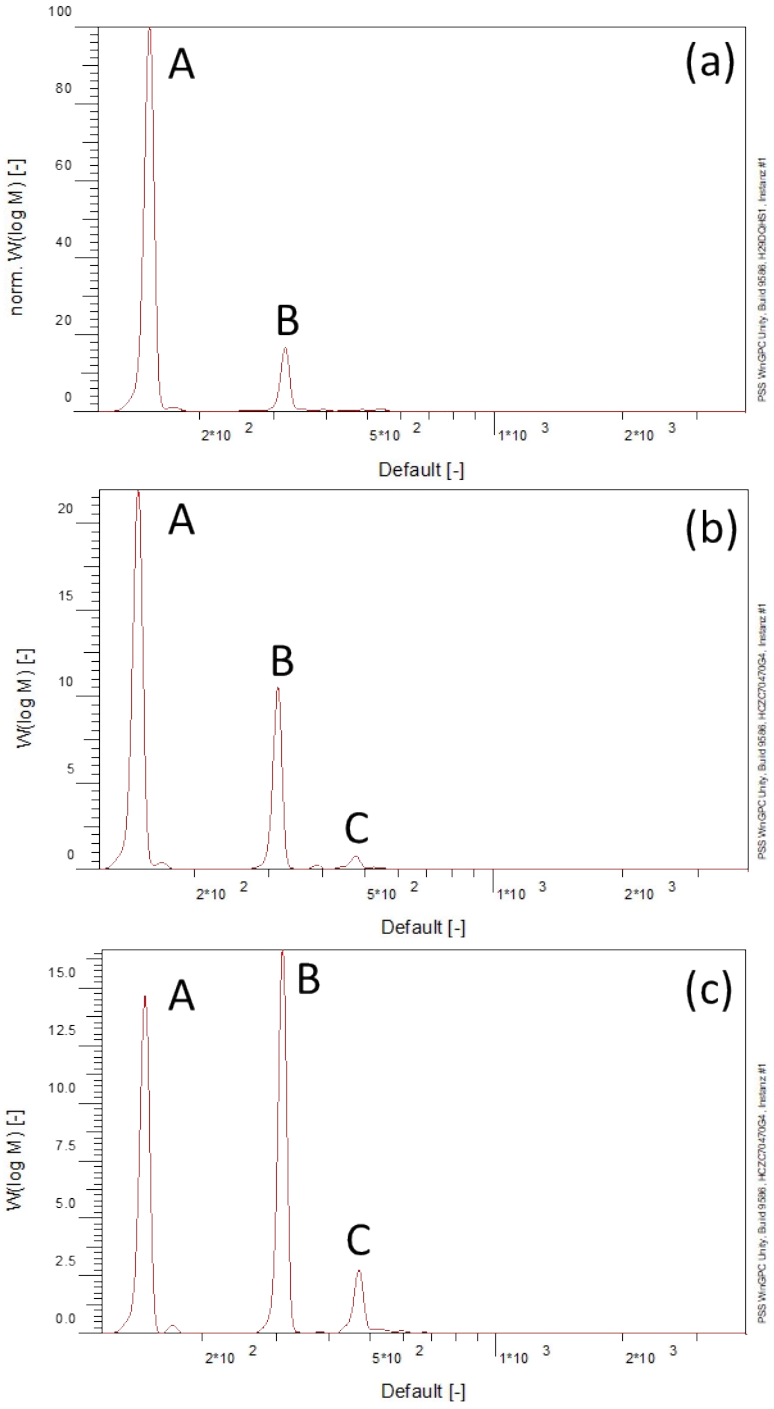

Fig. S1 GPC traces of reaction between 4,4'-MDI and 2-ethyl-1-hexanol in (a) 1:0.10; (b) 1:0.25; (c) 1:0.50 molar ratio.

Table S1 Molar percentage of different structures according to GPC results after reaction between 4,4'-MDI and 2-ethyl-1-hexanol in different molar ratio.

MDI:OH ratio	A Monomer	B mono-urethane	C di-urethane
1:0.10	0.90	0.10	0.00
1:0.25	0.77	0.21	0.02
1:0.50	0.58	0.37	0.05

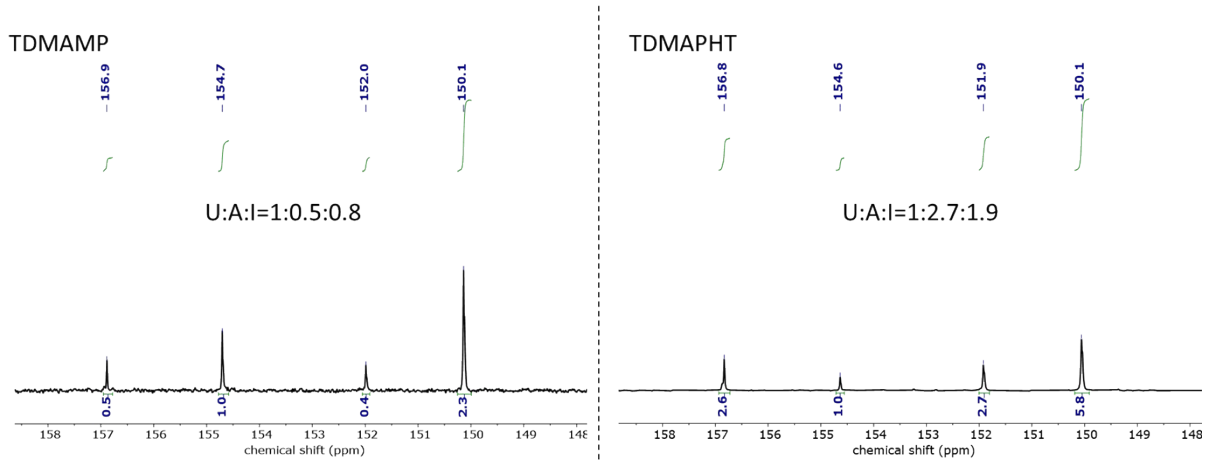

Fig. S2 ^{13}C NMR spectra (100MHz, acetone-d_6) of synthesized PIR prepolymer using TDMAMP or TDMAPHT as trimerization catalyst. The molar ratio of allophanate to isocyanurate was 0.6:1 and 1.4:1 respectively.

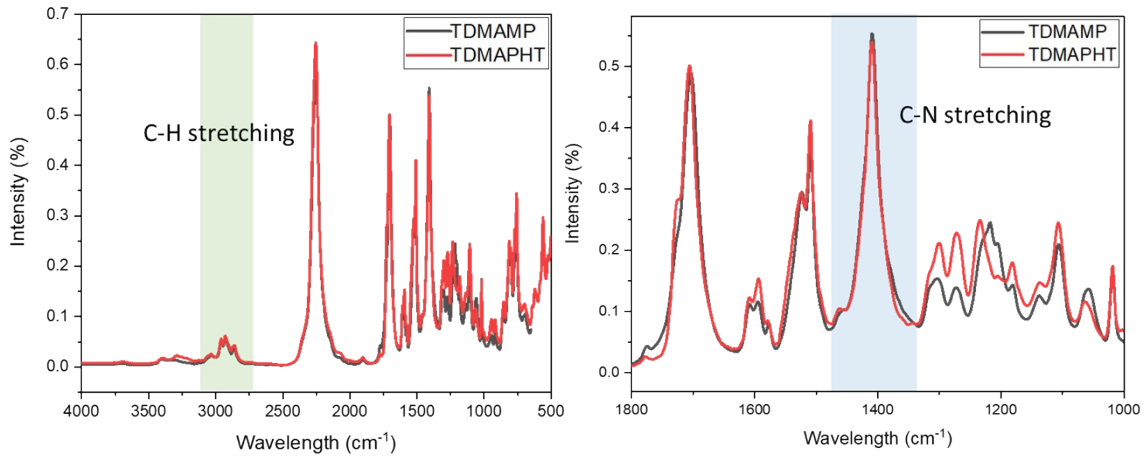

Fig. S3 FT-IR spectra of PIR prepolymer using TDMAMP or TDMAPHT as trimerization catalyst. After normalization based on the area of C-H stretching (3110-2770 cm^{-1}) of TDMAMP curve, the area of isocyanurate C-N stretching (1474-1338cm^{-1}) was 16.8 and 14.8 respectively, which means that more isocyanurate was formed when TDMAMP was used as trimerization catalyst.

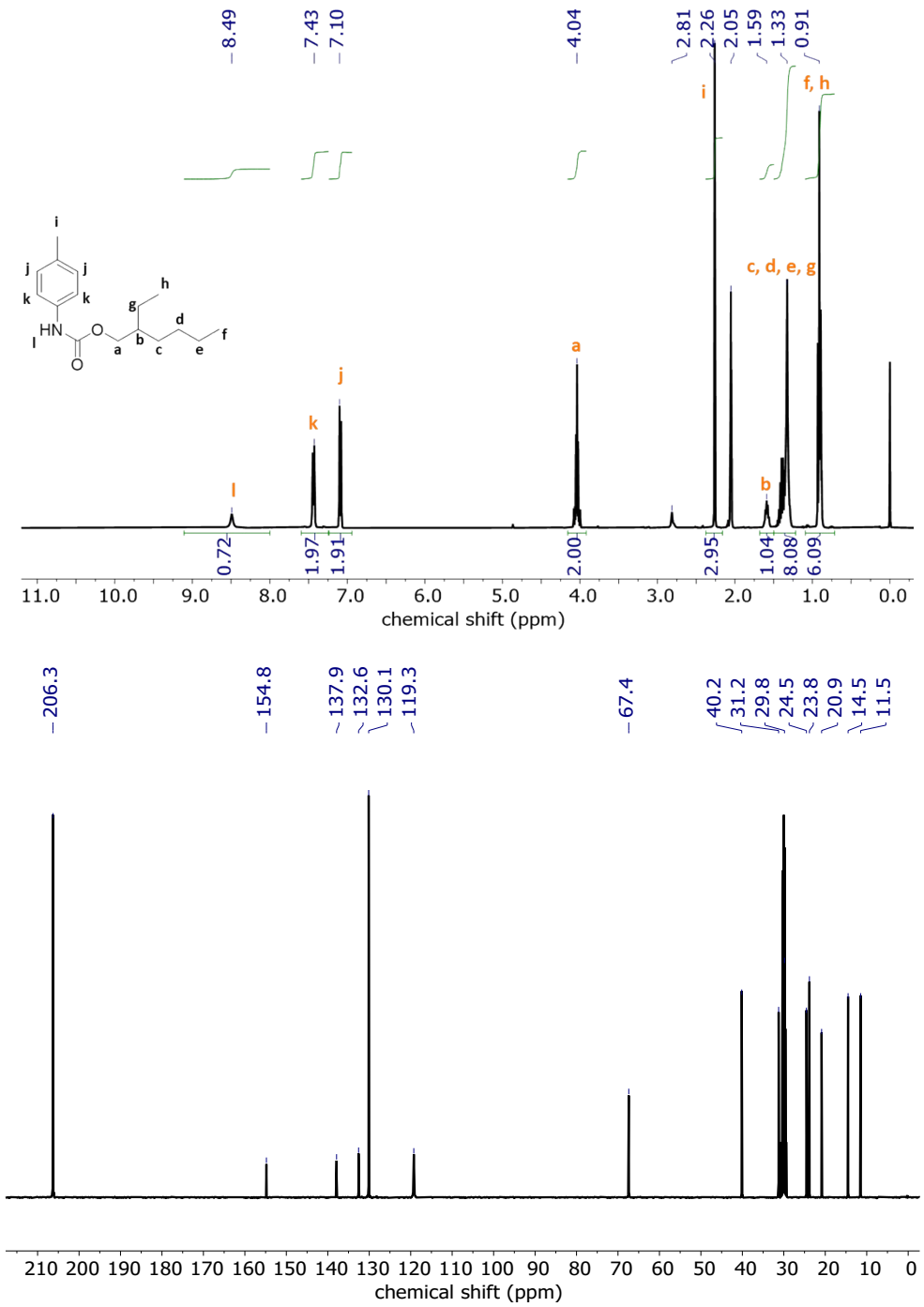

Fig. S4 ^{1}H NMR spectra (400 MHz, acetone-d_6) and ^{13}C NMR spectra (100 MHz, acetone-d_6) of 2-ethylhexyl *p*-tolylcarbamate.

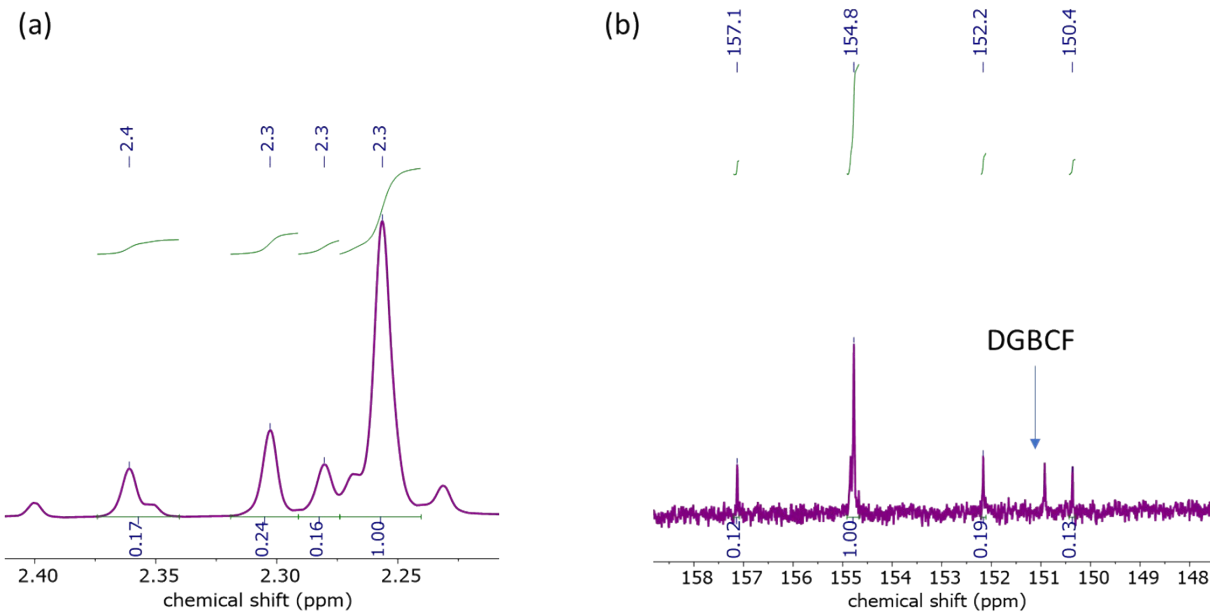

Fig. S5 (a) ^{1}H NMR spectra (400 MHz, acetone-d_6) and (b) quantitative ^{13}C NMR spectra (125 MHz, acetone-d_6) of product obtained from reaction between *p*-tolyl isocyanate and 2-ethylhexyl *p*-tolylcarbamate in 1:1 molar ratio in acetone-d_6 at 50 °C using 5 mol% TDMAMP as catalyst after 34 h.

According to the ^{1}H NMR spectra in Fig. S5a, the remaining allophanate can be calculated as: $\frac{0.16}{0.17/3 + 0.25 + 0.16 + (1 - 0.16)} = 12\ mol\%$.

Assume at t=0, there were 1mol urethane and 1mol isocyanate. At t=34 h, according to the ^{13}C NMR spectra in Fig. S5b, the molar ratio of urethane:allophante:isocyanurate is 1:0.16:0.04.

The obtained allophanate is $\frac{0.16}{1 + 0.16} \times 1mol = 0.14\ mol$, remaining urethane is $1 - 0.14 = 0.86\ mol$.

The obtained isocyanurate is $\frac{0.14}{0.16} \times 0.04 = 0.04\ mol$, remaining isocyanate is $1 - 0.14 \times 1 - 0.04 \times 3 = 0.74\ mol$.

Therefore, the remaining allophanate can be calculated as: $\frac{0.14}{0.14 + 0.86 + 0.04 + 0.74} = 8\ mol\%$.

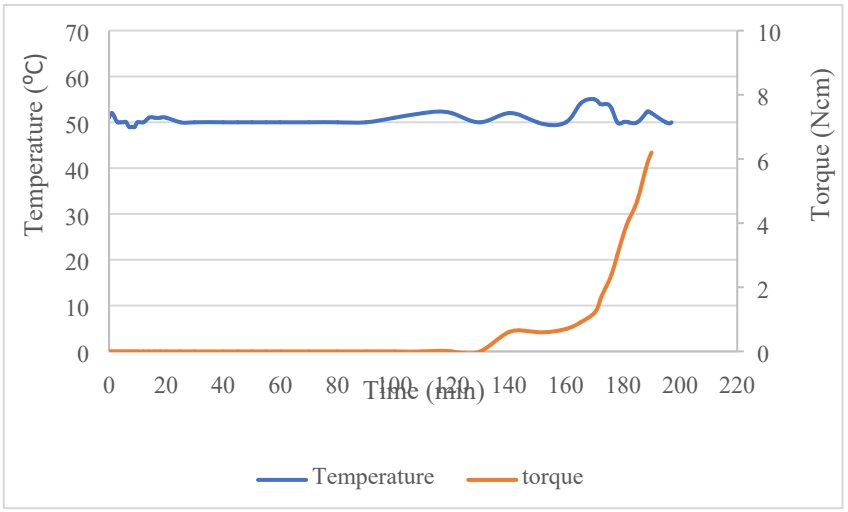

Fig. S6 Real-time temperature and torque during the synthesis of PIR prepolymer.

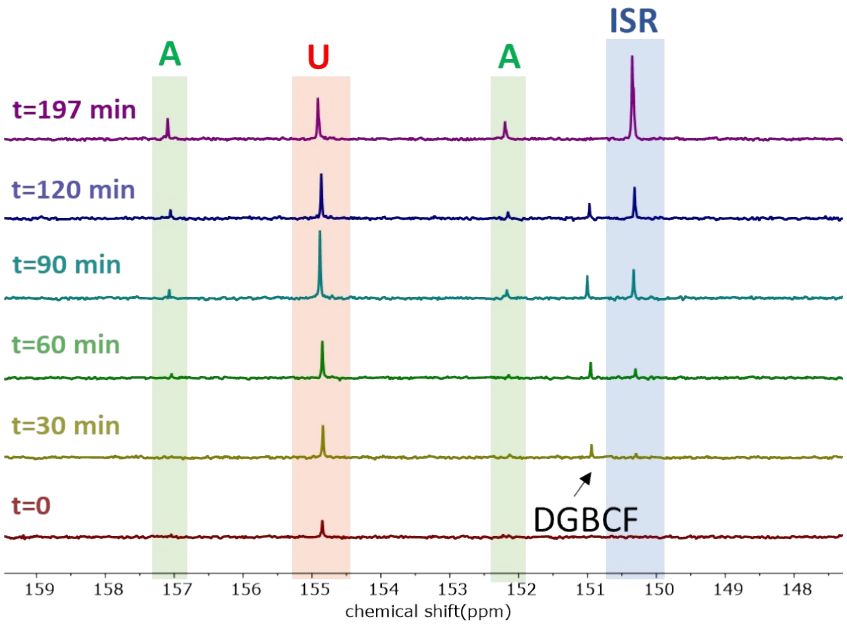

Fig. S7 ^{13}C NMR spectra (100 MHz, acetone-d_6) of the co-trimerization of mono- and di-functional isocyanates. U (carbamate); A (allophanate); ISR (isocyanurate).

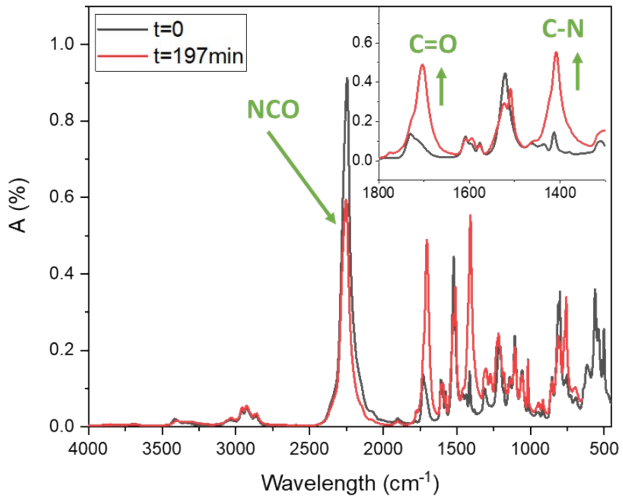

Fig. S8 FT-IR spectra of PIR prepolymer.

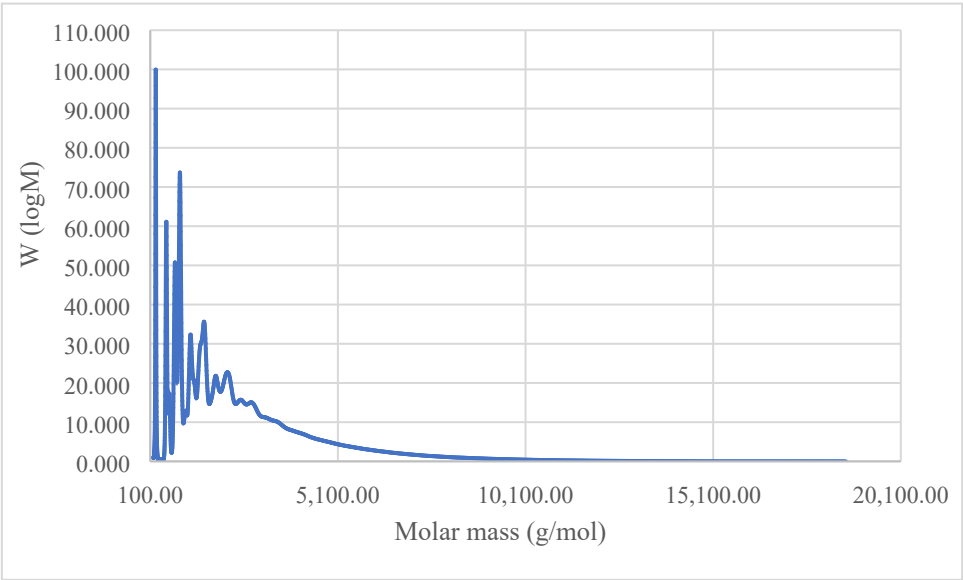

Fig. S9 GPC trace of PIR prepolymer, obtained M_n=660 g/mol.

Based on the GPC result, the functionality of the PIR-DEHP prepolymer can be calculated using the following equation:

$$NCO\ content = \frac{f_n \times n_{prepolymer} \times M_{NCO}}{n_{prepolymer} \times M_{prepolymer}},$$

$$f_n = \frac{NCO\ content\ \times n_{prepolymer} \times M_{prepolymer}}{n_{prepolymer}\ \times\ M_{NCO} \times 100wt\%} = \frac{16\ wt\% \times 660\ g/mol}{42 g/mol \times 100wt\%} = 2.5,$$

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

2. Preparation of elastomers in solution

Table S2 Recipes (by weight percentage) of solution-casted elastomers (Index 105).

	PIR elastomers				**4,4'-MDI based elastomer**	**M20 elastomers**	
BDO in polyol component	0% BDO	5% BDO	10% BDO	15% BDO	15% BDO	0% BDO	15% BDO
PIR prepolymer	21.7	36.3	46.3	53.6	--	--	--
4,4'-MDI	--	--	--	--	35.4	--	--
M20	--	--	--	--	--	12.3	36.9
PTHF/ PESOL	78.3	60.5	48.3	39.4	54.9	87.7	53.6
BDO	--	3.2	5.4	7.0	9.7	--	9.5

The PIR prepolymer is trimerized from a mixture containing 184 g 4,4'-MDI and 24 g 2-ethyl-1-hexanol, which means that there is 88.5 wt% isocyanate contained in PIR prepolymer. The aromatic content of PIR elastomers with 15% BDO, for example, can be calculated as: 53.6%×88.5%=47%. The aromatic content of 4,4'-MDI based elastomer and M20 elastomers is the amount of isocyanate that was used.

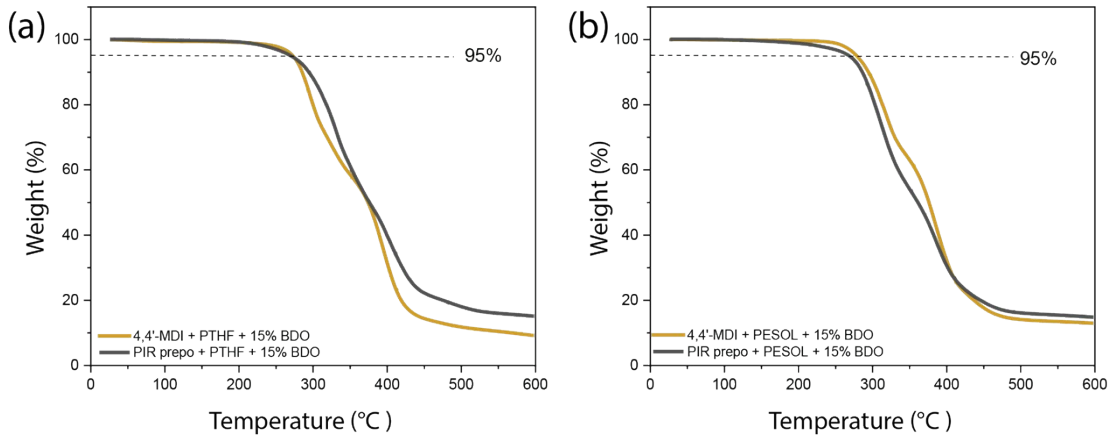

Fig. S10 TGA curves of PIR elastomers compared to classical elastomers which are obtained from the reaction of 4,4'-MDI, polyol and BDO without trimerization. All the elastomers contain 15 wt% BDO (a: PTHF-containing; b: PESOL-containing).

Table S3 TGA results of PIR elastomers compared to classical elastomers which are obtained from reaction of 4,4'-MDI, polyol and BDO without trimerization.

	Aromatic content* **(wt%)**	**T_{d5} (°C)**	**T_{d10}(°C)**	**Char at 596 °C (%)**
PIR prepo + PTHF +15% BDO	47	270.1	294.2	15.2
4,4'-MDI + PTHF + 15% BDO	35	272.7	285.2	9.3
PIR prepo + PESOL + 15% BDO	47	268.5	286.2	14.9

4,4’-MDI + PESOL + 15% BDO	35	278.5	294.5	13.0

*The aromatic content is calculated based on the weight percentage of aromatic isocyanate in the elastomers.

3. Preparation of elastomers in bulk

Table S4 Recipes (by weight percentage) of bulk-cast elastomers (Index 105).

	PIR			**M20**
BDO in polyol component	5 wt% BDO	10 wt% BDO	15 wt% BDO	15 wt% BDO
PIR prepolymer	35.5	45.5	52.8	--
M20	--	--	--	36.9
PESOL	61.3	49.1	40.1	53.6
BDO	3.2	5.4	7.1	9.5