Supporting Information

Alkoxyamine with reduced homolysis temperature and its application in repeated autonomous self-healing of stiff polymer

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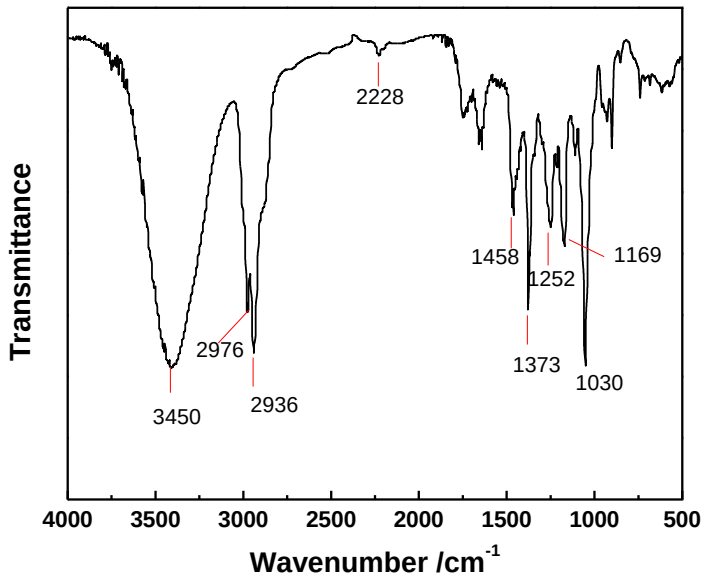


Figure S1. FTIR spectrum of CTPO with the following characteristic peaks demonstrating its chemical structure: 3450 cm^{-1} (O-H bond), 2976 and 2936 cm^{-1} ($-CH_3$ and $-CH_2$ stretching), 2228 cm^{-1} (-C≡N stretching), 1458 cm^{-1} ($-CH_3$ bending), 1373 and 1360 cm^{-1} ($-CH_3$ anti-symmetric bending), 1252 cm^{-1} (C-N stretching), 1169 cm^{-1} (C-O-N anti-symmetric stretching), and 1033 cm^{-1} (C-OH stretching).

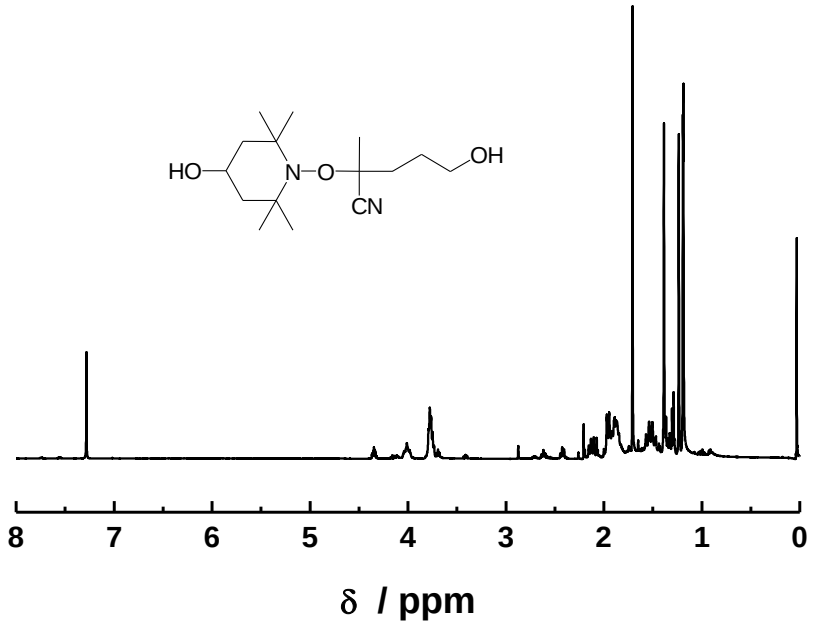


Figure S2. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25 °C) of CTPO with the following characteristic peaks demonstrating its chemical structure: δ (ppm) = 7.283 ($CDCl_3$), 1.188 (TEMPOL C*H*$_3$), 1.193 (TEMPOL C*H*$_3$), 1.235 (TEMPOL C*H*$_3$), 1.386 (TEMPOL C*H*$_3$), 1.708 (-CN-C-C*H*$_3$), 1.386-1.999 (TEMPOL C*H*$_2$), 1.999-2.206 (-C*H*$_2$-C*H*$_2$-), 3.763 (-OH-C*H*$_2$-CH$_2$-), and 3.991 (-OH-C*H*-(CH$_2$)$_2$-). The latter two clearly prove the structure of this monomer.

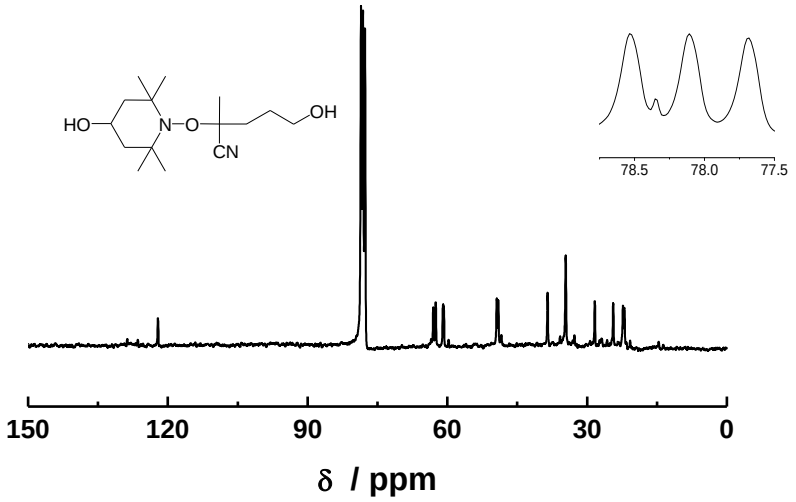


Figure S3. ^{13}C NMR spectrum (300 MHz, $CDCl_3$, 25 °C) of CTPO with the following characteristic peaks: δ/ppm 22.29-24.18 (TEMPOL *C*H$_3$), 34.71 (-CN-C-*C*H$_3$), 38.62-49.54 (-*C*H$_2$-CH$_2$-, -CH$_2$-*C*H$_2$-), 60.74 (-CH$_2$-*C*-NO-), 62.19 (CH$_2$-*C*H$_2$-OH), 63.01 (-OH-*C*H-(CH$_2$)$_2$-), 78.34 (-NO-*C*-CN, partially overlapped with the triplet peaks of $CDCl_3$), and 128.28 (*C*≡N).

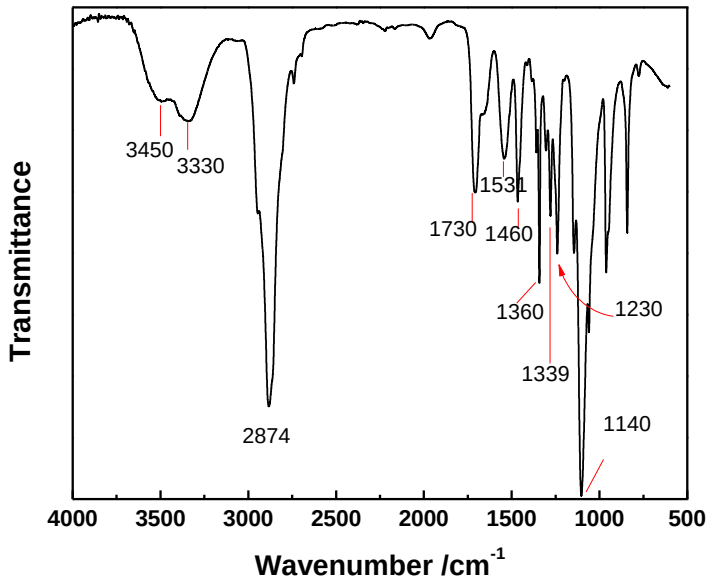


Figure S4. FTIR spectrum of ICPEG2000 with the following characteristic peaks: 3450 cm^{-1} (N-H hydrogen bonding), 3330 cm^{-1} (N-H free), 2874 cm^{-1} (-CH_3 and CH_2 stretching), 1730 cm^{-1} (C=O hydrogen bonding), 1664 cm^{-1} (C=O free), 1531 cm^{-1} (N-H bending and C-N stretching), 1460 cm^{-1} (-CH_3 and –CH_2 bending), 1360 cm^{-1} (-CH_3 anti-symmetric bending), 1339 cm^{-1} (N-O stretching), 1230 cm^{-1} (N-H bending vibration and C-N stretching), and 1140 cm^{-1} (C-O-C anti-symmetric stretching). *Note: The peaks at 3450 and 3330 cm^{-1} are assigned to -NH in hydrogen bonding and free -NH groups, respectively. The hydrogen bonding is constituted by -NH groups (acting proton donors) and oxygen (in carbonyls of the hard segment and ethers of the soft segment as proton acceptors). Analogously, the peak position at 1730 cm^{-1} is ascribed to hydrogen bonded -C=O and the shoulder peak at 1664 cm^{-1} to free -C=O. The FTIR spectrum also indicates completion of the reaction between diisocyanate and polyol owing to the disappearance of the NCO absorption band at 2270 cm^{-1}. N-H bending and C-N stretching at 1531 cm^{-1}, N-H bending and C-N stretching at 1230 cm^{-1}, N-O stretching at 1339 cm^{-1} and C-O-C stretching at 1140 cm^{-1} are also observed. The spectrum shows no absorption at 1650 cm^{-1} for urethane-urea formation, implying that the polymer is a kind of thermoplastic material without branched or crosslinking structure.*

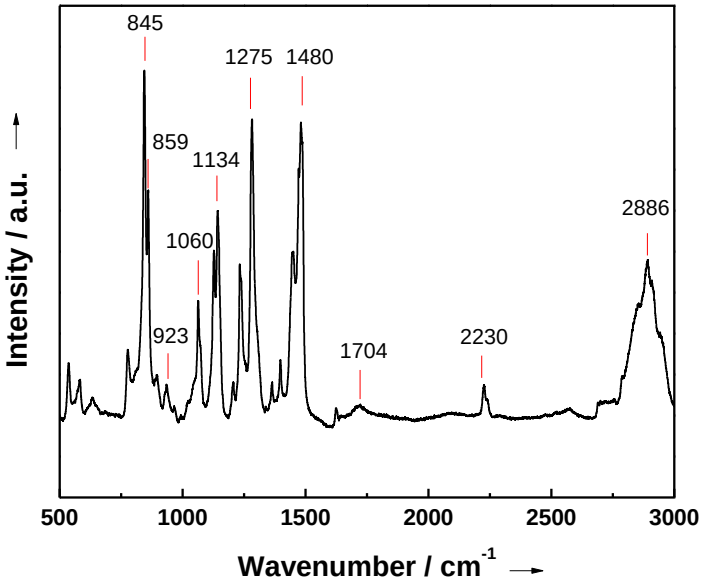
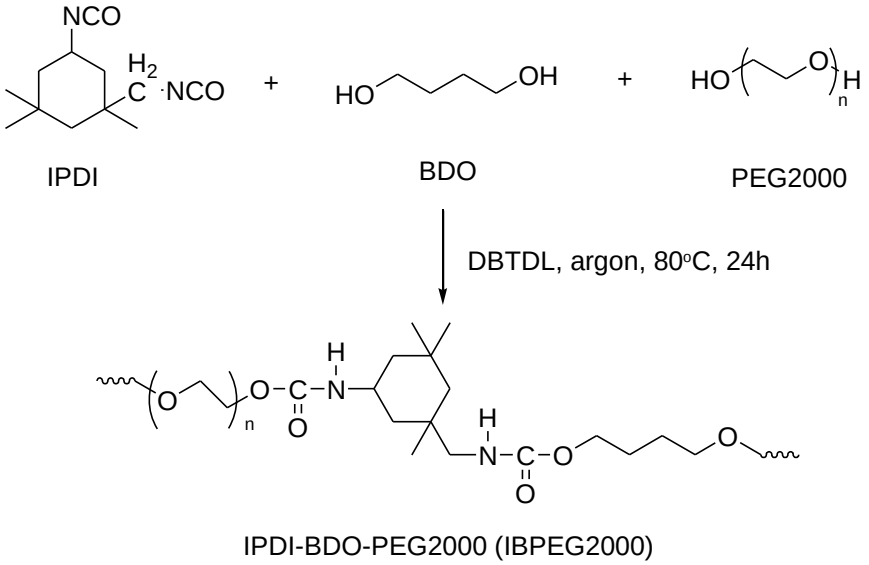


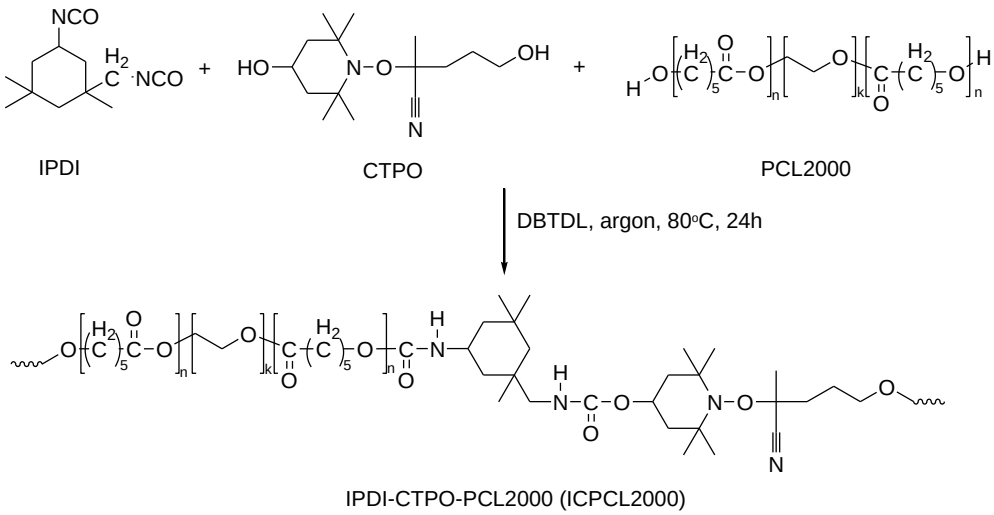
Figure S5. Raman spectrum of ICPEG2000 with the following characteristic peaks: 2886 cm^{-1} (-CH_3 and CH_2 stretching), 2230 cm^{-1} (-CN stretching), 1704 cm^{-1} (C=O stretching), 1480 cm^{-1} (N-H bending), 1275 cm^{-1} (C-N stretching), 1134 cm^{-1} (C-O-C anti-symmetric stretching), 1060 cm^{-1} (C-O anti-symmetric stretching), 923 cm^{-1} (O-N stretching), 859 cm^{-1} (C-O-C symmetric stretching and C-O-N pseudo-symmetry stretching), and 845 cm^{-1} (C-O symmetric stretching). *Note: It is obvious that 2230 cm^{-1} peak belongs to –CN according to the Raman spectroscopy result and the outcome of FTIR spectrum. The ether oxygen region between 1200 and 1000 cm^{-1} contains C-O-C anti-symmetric stretching of PEG soft segment (1134 cm^{-1}) and C-O anti-symmetric stretching (~1060 cm^{-1}). The peak at 1704 cm^{-1} originates from C=O symmetric stretching vibration (amide I band) of carbonate groups, while those at 1480 and 1275 cm^{-1} are due to N-H bending (amide II band) and C-N (amide III band) stretching. Additionally, O-N stretching at 923 cm^{-1}, C-O symmetric stretching at 845 cm^{-1}, C-O-C anti-symmetric stretching and C-O-N pseudo-symmetry stretching at 859 cm^{-1} are also observed.*

The control material that excludes alkoxyamine moiety, IBPEG2000, was made following similar procedures by using BDO instead of CTPO monomer (**Scheme S1**).



Scheme S1. Synthesis of irreversible polyurethane IBPEG2000.

When PEG2000 diol was replaced by PCL2000 diol, ICPCL2000 can be prepared by the similar process (**Scheme S2**). The chemical structure of the product was also proved by FTIR spectrum (**Figure S6**).



Scheme S2. Synthesis of reversible polyurethane ICPCL2000.

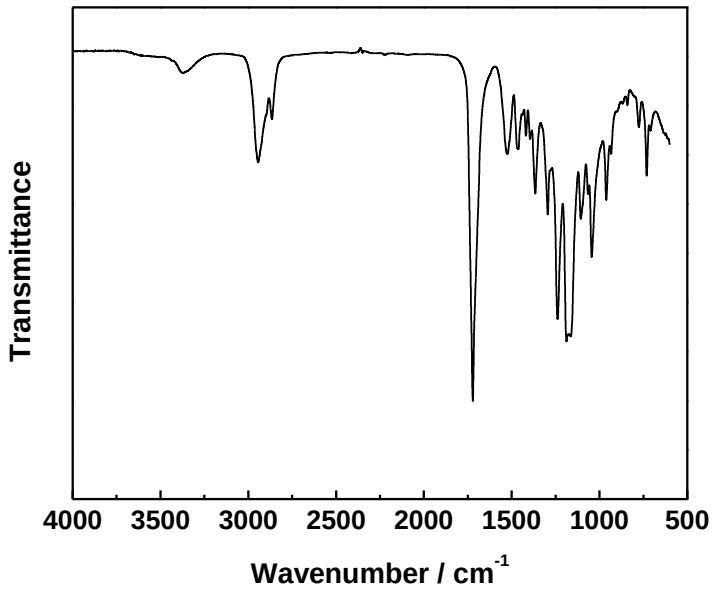


Figure S6. FTIR spectrum of ICPCL2000 with the following characteristic peaks:3360 cm^{-1} (N-H bond), 2947, 2867 cm^{-1} (-CH_3 and CH_2 stretching), 1723 cm^{-1} (C=O stretching), 1528 cm^{-1} (N-H bending and C-N stretching), 1461 cm^{-1} (-CH_3 and –CH_2 bending), 1367 cm^{-1} (-CH_3 anti-symmetric bending), 1293 cm^{-1} (N-O stretching), 1232 cm^{-1} (N-H bending vibration and C-N stretching), 1172 cm^{-1} (C-O stretching), and 1104 cm^{-1} (C-O-C stretching). *Note: The 3360 cm^{-1} peak is assigned to -NH in hydrogen bonding, meaning that almost all the -NH groups act as proton donor to constitute the hydrogen bonding. ICPCL2000 has seldom free -NH groups because the PCL soft segments contain lots of ester groups to serve as proton acceptors, which differ from ICPEG2000. The peak at 1760 cm^{-1} is ascribed to hydrogen bonded -C=O of carbonate groups and ester groups. According to the disappearance of the NCO absorption band at 2270 cm^{-1}, we can predicate the reaction between diisocyanate and polyol is fully completed. In addition, N-H bending and C-N stretching at 1528 cm^{-1}, N-H bending and C-N stretching at 1232 cm^{-1}, N-O stretching at 1293 cm^{-1}, C-O stretching at 1172 cm^{-1} and C-O-O stretching at 1104 cm^{-1} are also observed.*

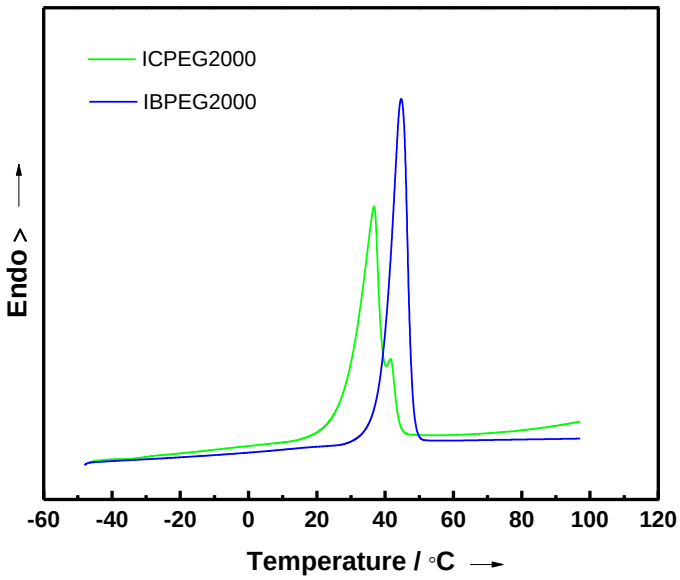


Figure S7. DSC heating scans of ICPEG2000 and IBPEG2000.

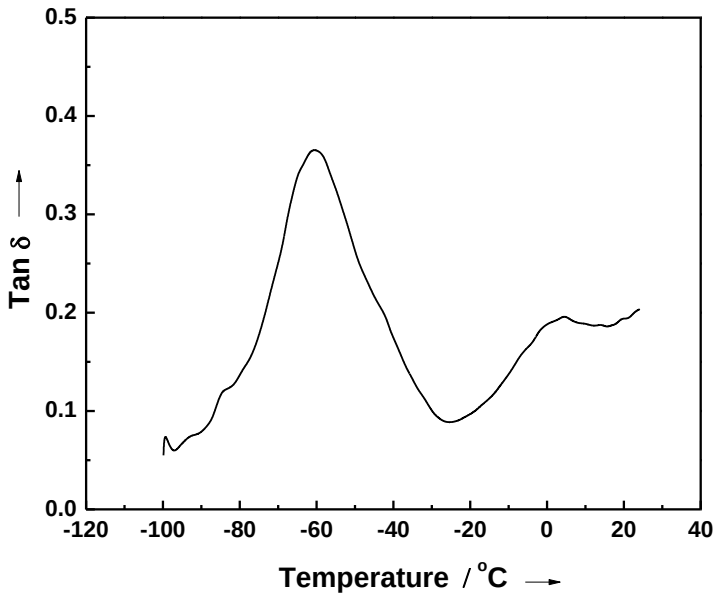
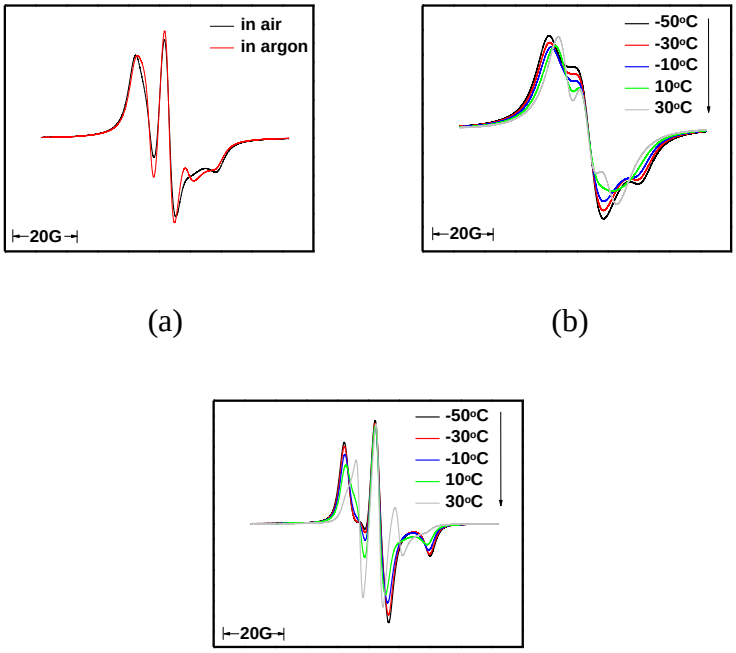


Figure S8. Tan δ versus temperature of ICPEG2000.

Table S1. Radical concentrations in TEMPO and CTPO determined by titration

Sample and test temperature		W_0[a] (g)	V_1[b] (ml)	V_2[c] (ml)	C_1[d] (mN g^{-1})	C_2[e] (mN g^{-1})
TEMPO	-30 °C	0.1752	11.44	21.68	2.922	2.918
	-30 °C	0.1733	11.58		2.914	
	30 °C	0.1755	10.75	21.28	3.000	2.999
	30 °C	0.1717	10.98		2.999	
CTPO	-30 °C	0.5201	20.19	21.12	0.089	0.0895
	-30 °C	0.4765	20.26		0.090	
	30 °C	0.5197	17.26	20.45	0.307	0.3035
	30 °C	0.4198	17.93		0.300	

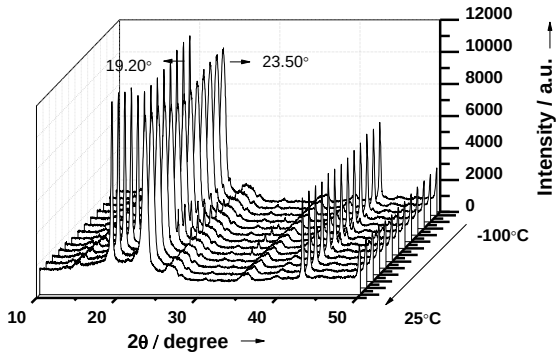
[a]W_0 = sample weigh; [b]V_1 = volume of iodine solution used for titration of the sample; [c]V_2 = volume of iodine solution used for titration of the blank experiment; [d]C_1 = radical concentration; [e]C_2 = average radical concentration. *Note: Free radical concentrations of TEMPO and CTPO at different temperatures (-30 ~ 30 ℃) are determined by titration, which quantifies fission behavior of CTPO. During the measurements, nitroxide and carbon radicals are reduced by ascorbic acid, while ascorbic acid is oxidized. For stable nitroxide radicals of TEMPO, the measured radical concentration keeps constant at both -30 and 30 ℃. In contrast, the amount of free radicals of CTPO at -30 ℃ is only about 30 % of that measured at 30 ℃, demonstrating that fission of C-ON bonds indeed happens at ambient temperature.*



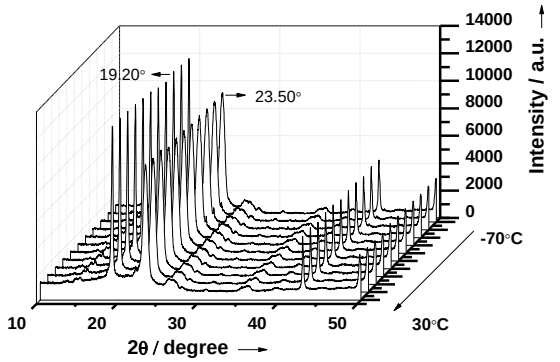
(a) (b)

(c)

Figure S9. (a) Typical ESR spectra of ICPEG2000 measured at 30 °C in argon and air, respectively. Typical ESR spectra measured at various temperatures of (b) CTPO and (c) ICPEG2000, which had been stored at ambient temperature in air for a week and 6 months, respectively.

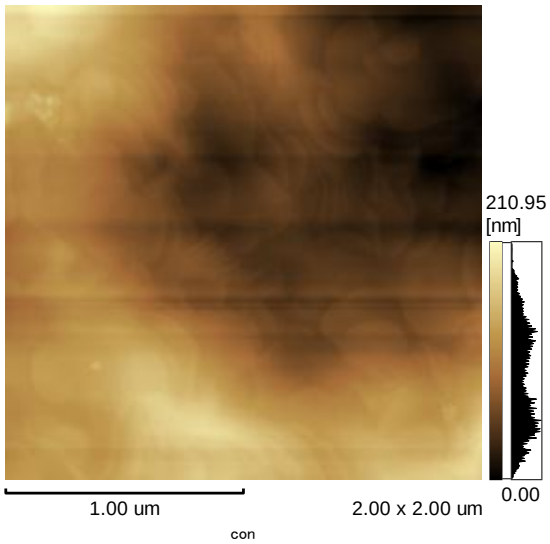


(a)

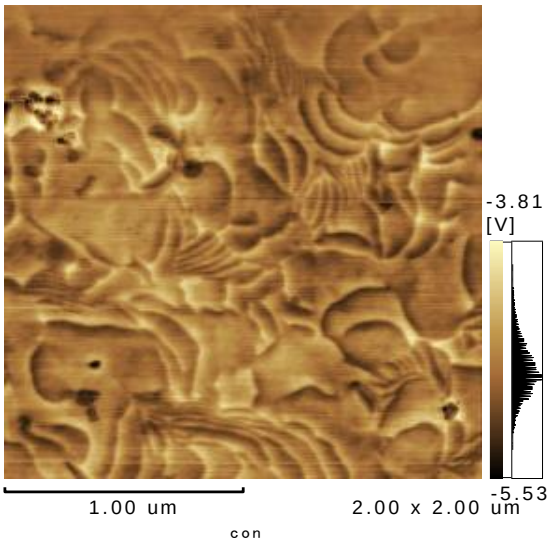


(b)

Figure S10. Temperature dependences of wide angle X-Ray diffraction patterns of (a) ICPEG2000 and (b) IBPEG2000.



(a)



(b)

Figure S11. AFM high-contrast (a) and phase-contrast (b) image of ICPEG2000.

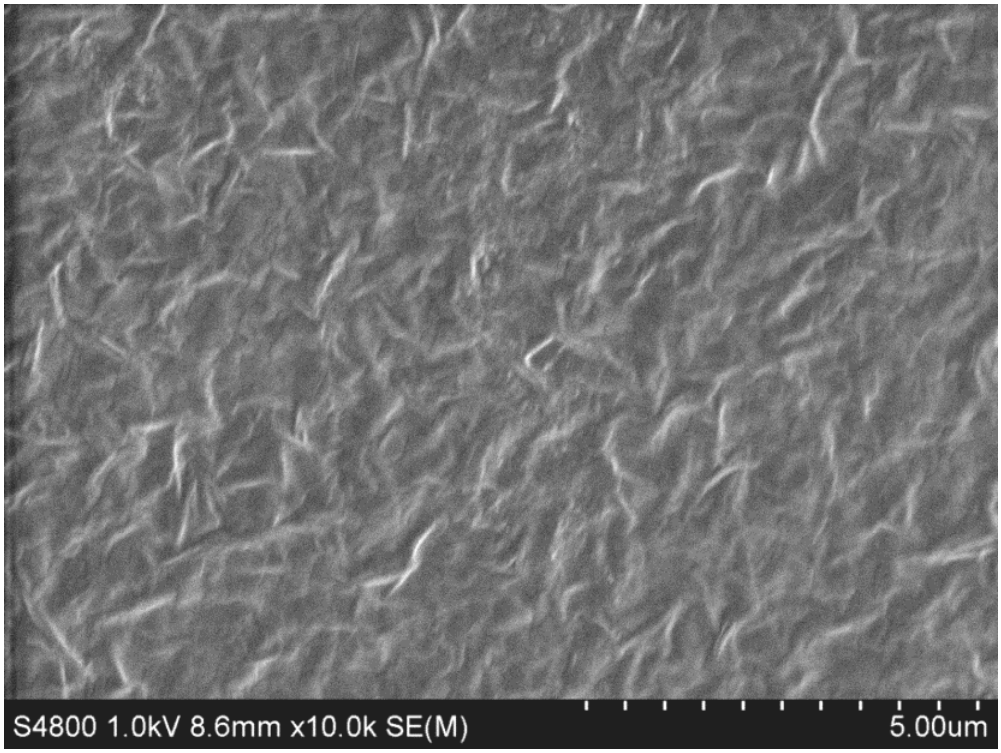


Figure S12. SEM image of ICPEG2000.

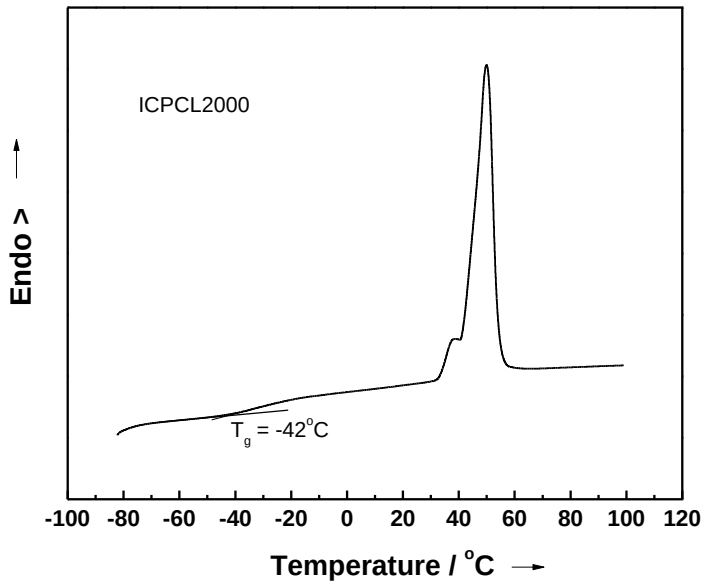


Figure S13. DSC heating scan of ICPCL2000.

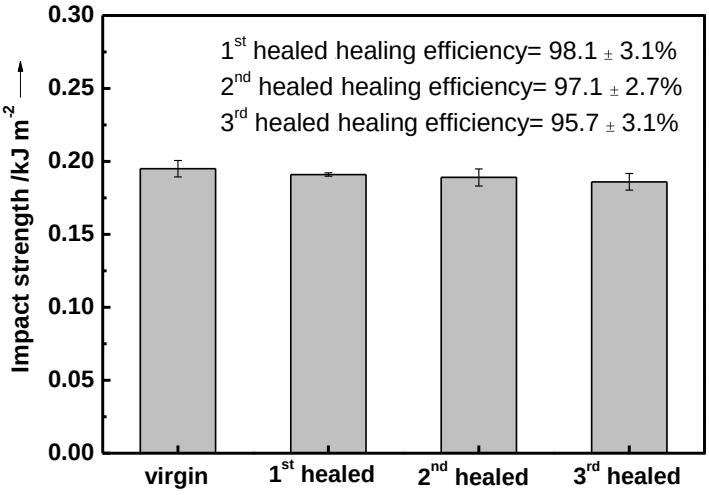


Figure S14. Impact strengths of virgin ICPCL2000 specimens and the repeatedly healed versions. Temperature of impact test and crack healing: 15 °C. Healing time and atmosphere: 48 h, air.