Supplementary Information

Thermally remendable and reprocessable crosslinked methyl methacrylate polymer based on oxygen insensitive dynamic reversible C-ON bonds

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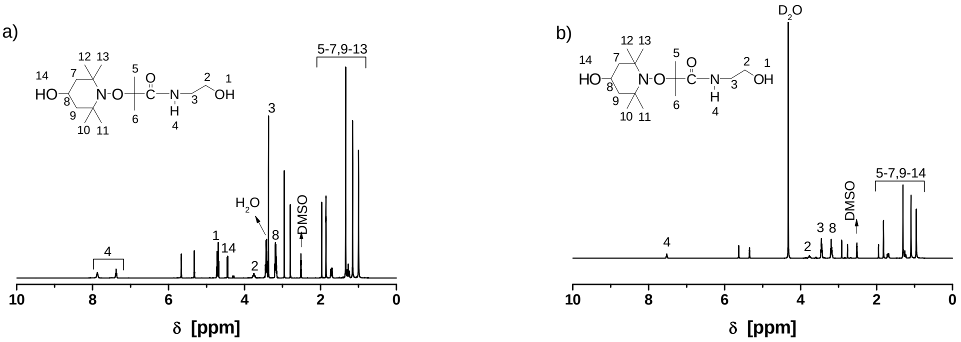


Fig. S1 ^{1}H NMR spectra of Diol in (a) DMSO-d6 and (b) DMSO-d6 with D_2O.

^{1}H NMR (400 MHz, DMSO, 25 °C, δ/ppm) with the following characteristic peaks demonstrating its chemical structure: 0.998, 1.154, 1.337, 1.701, 1.853, 1.969, 3.151, 3.370, 3.760, 4.444, 4.712, 7.394 and 7.874. 0.998~1.969 (complex, 23H, CH_3, CH_2, and CH of the TEMPO group, CH_3 linked to quaternary carbon atom), 3.151 (1H, HO-CH-$(CH_2)_2$), 3.370 (2H, -CO-NH-CH_2), 3.760 (2H, CH_2-CH_2-OH), 4.444 (1H, reactive hydrogen of -OH connect to TEMPO group) and 4.712 (1H, reactive hydrogen of another -OH), 7.394 (1H, reactive hydrogen of amido, hydrogen bond), and 7.874 (1H, reactive hydrogen of amido, non-hydrogen bond). By comparing the spectra before and after deuterium oxide exchange, it is found that the signals of active hydrogen become weakened or even disappear, but that of amido is still detected owing to the slow exchange speed of amido.

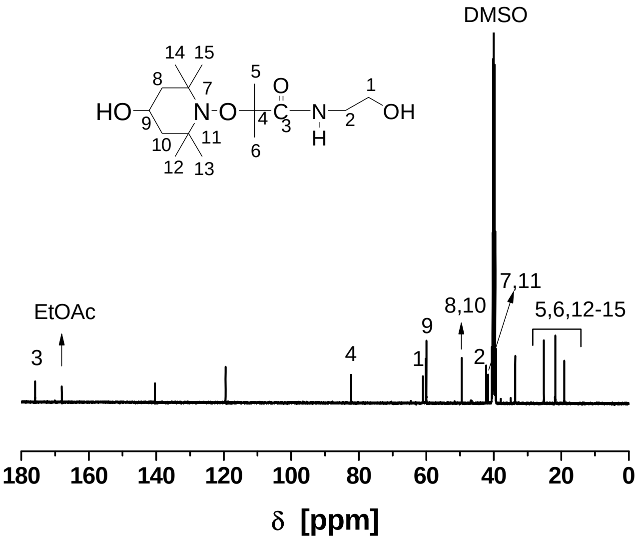


Fig. S2 ^{13}C NMR spectrum of Diol in DMSO-d6.

^{13}C NMR (400MHz, DMSO, 25 °C, δ/ppm) with the following characteristic peaks: 175.824 (C=O), 167.617 (C=O of solvent EtOAc), 82.241 (-O-*C*-C=O), 61.275 (-CH$_2$-*C*H$_2$-OH)，59.922 (-*C*H of TEMPO group which linked to -OH), 49.510 (*C*H$_2$ of the TEMPO group), 42.260 (-NH-*C*H$_2$-CH$_2$), 39.761 and 41.703 (-CH$_2$-*C*-NO of the TEMPO group), 25.087 (-*C*H$_3$-C-TEMPO), and 21.544.12-19.732 (*C*H$_3$ of the TEMPO group).

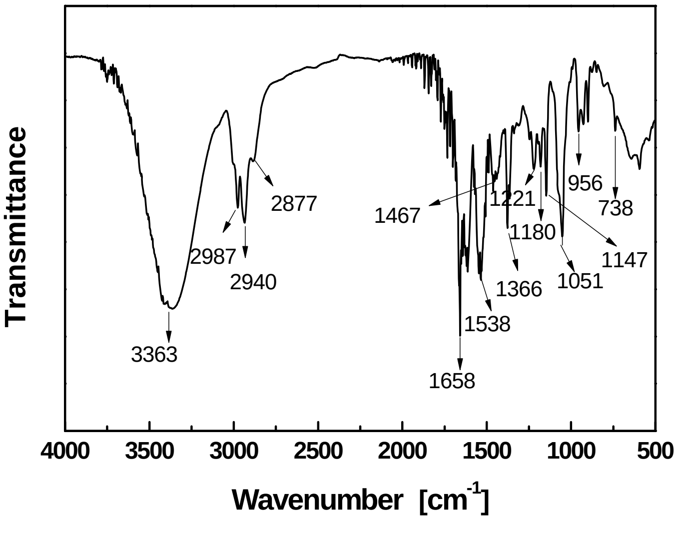


Fig. S3 FTIR spectrum of Diol.

FTIR spectrum (KBr) of Diol with the following characteristic peaks: 3363 cm^{-1} (-OH hydrogen bonding), 2987-2877 cm^{-1} (-CH$_3$ and CH$_2$ stretching), 1658 cm^{-1} (C=O free), 1538 cm^{-1} (C-N-H bending stretching),1467 cm^{-1} (-CH$_2$ bending), 1377 and 1365cm^{-1} (-CH$_3$ anti-symmetric bending), 1310 cm^{-1} (C-N stretching and C-H bending), 1221 cm^{-1} (N-O stretching of alkoxyamine), 1180 cm^{-1} (C-N stretching), 1147 cm^{-1} (C-O-N stretching), 1052 cm^{-1} (C-O stretching), 956 cm^{-1} (piperidine ring, bending), and 738 cm^{-1} (N-H out-of-plane bending).

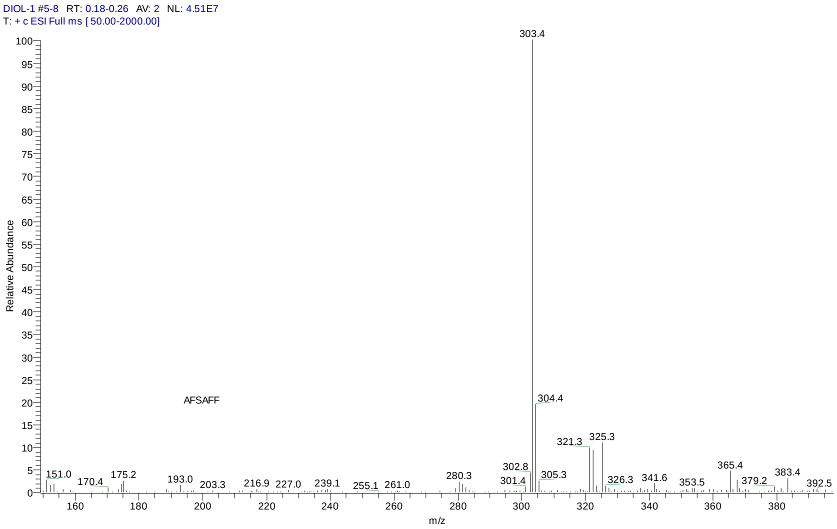


Fig. S4 EI-MS spectrum of Diol.

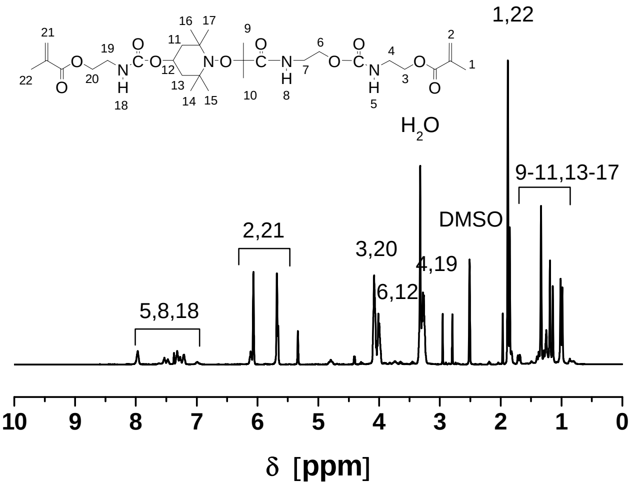


Fig. S5 ^{1}H NMR spectrum of Dima in DMSO-d6.

^{1}H NMR (400MHz, DMSO, 25^{o}C, δ/ppm) with the following characteristic peaks demonstrating its chemical structure: 0.986, 1.190, 1.336, 1.717, 1.886, 1.966, 3.281, 3.997, 4.011, 4.082, 5.681, 6.067, 7.208-7.530, 7.969. 0.986-1.966 (complex, 27H, CH_3 and CH_2 of the TEMPO group, CH_3 linked to quaternary carbon atom, CH_3 linked to ethylene linkage), 3.281 (4H, -OOC-NH-C*H₂*), 3.997 (1H, -C*H* of the TEMPO group), 4.011 (2H, -C*H₂*-COO-NH), 4.082 (2H, -C*H₂*-OOC-), 5.681 and 6.067 (4H, =C*H₂*), 7.208-7.530 (3H, reactive hydrogen of amido, hydrogen bond), and 7.969 (3H, reactive hydrogen of amido, non-hydrogen bond).

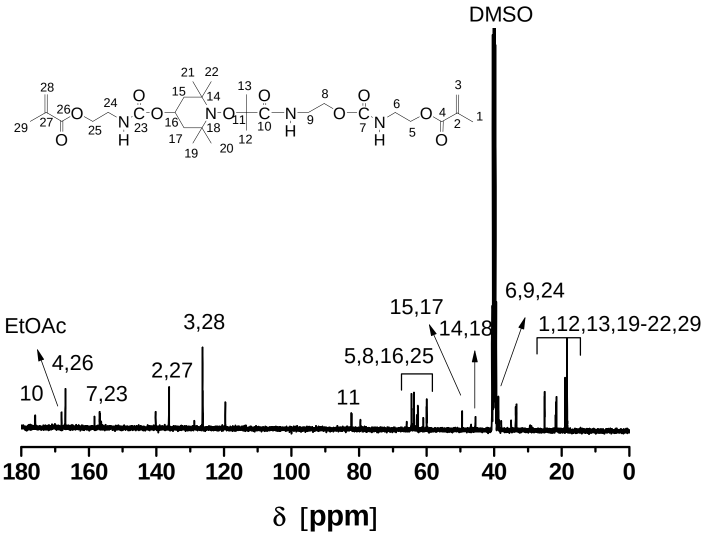


Fig. S6 ^{13}C NMR spectrum of Dima in DMSO-d6.

^{13}C NMR (400MHz, DMSO, 25°C, δ/ppm) with the following characteristic peaks: 176.101 (C-*C*=O-NH-), 166.866 (-O-*C*=O- of methacrylate ester), 158.427 and 156.253 (carbamate groups), 136.375 and 126.589 (-*C*=*C*- of methacrylate ester), 126.589 (-O-*C*=O- of methacrylate ester), 82.199 (-O-*C*-C=O), 64.515 and 63.455 (-CH_2 connect to oxygen atom of methacrylate ester)，62.573 and 59.920 (-CH_2 and -*C*H connect to carbamate groups), 49.581 (-CH_2 of TEMPO group), 45.770 (-*C* - of the TEMPO group), 39.011 (-CH_2 connect to nitrogen atom of carbamate groups), 38.753 (-CH_2 connect to nitrogen atom of amido), 25.090 (-CH_3-C-TEMPO), 21.847.12-19.147 (CH_3 of the TEMPO group), and 18.309 (-CH_3 of methacrylate ester).

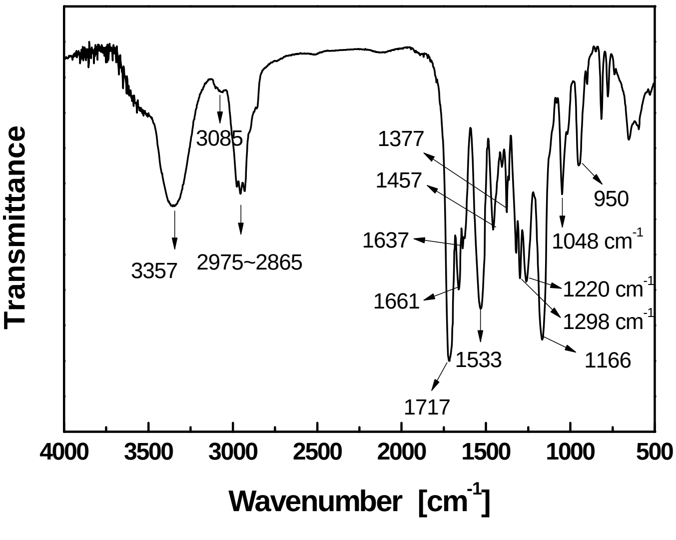


Fig. S7 FTIR spectrum of Dima.

FTIR spectrum (KBr) of Dima with the following characteristic peaks: 3357 cm^{-1} (-NH-stretching of amido and carbamate groups), 3085 cm^{-1} (=CH stretching), 2975-2865 cm^{-1} (-CH$_3$ and CH$_2$ stretching), 1717 cm^{-1} (C=O of ester and carbamate groups), 1661 cm^{-1} (C=O of amido group), 1637 cm^{-1} (C=C stretching), 1533 cm^{-1} (C-N-H bending stretching), 1457 cm^{-1} (-CH$_2$ bending), 1376cm^{-1} (-(CH$_3$)$_2$anti-symmetric bending), 1321 cm^{-1} (-CH$_3$ anti-symmetric bending), 1298 cm^{-1} (C-N stretching and C-H bending), 1260 cm^{-1} (N-O stretching of alkoxyamine), 1220 cm^{-1} (C-N stretching), 1166 cm^{-1} (C-O-C stretching), 1048 cm^{-1} (C-O stretching), 950 cm^{-1} (piperidine ring, bending), and 738 cm^{-1} (N-H out-of-plane bending).

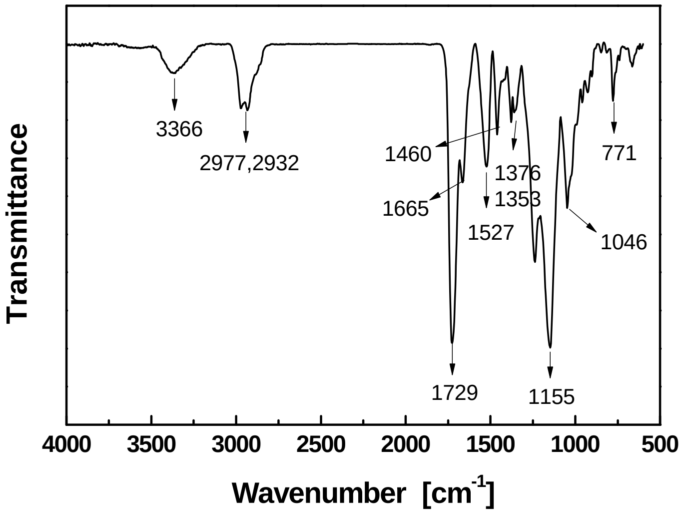


Fig. S8 FTIR spectrum of Dima/TMPMP.

FTIR spectrum (KBr) of Dima/TMPMP with the following characteristic peaks: 3366 cm^{-1} (-NH stretching), 2977-2932 cm^{-1} (-CH$_3$ and CH$_2$ stretching), 1729 cm^{-1} (-C=O of ester and carbamate groups), 1665 cm^{-1} (C=O of amido group), 1527 cm^{-1} (C-N-H bending stretching), 1460 cm^{-1} (-CH$_2$ bending), 1376 cm^{-1} (-(CH$_3$)$_2$ anti-symmetric bending), 1353 cm^{-1} (-CH$_3$ anti-symmetric bending), 1155 cm^{-1} (C-O-C stretching), 1046 cm^{-1} (C-O stretching), and 771 cm^{-1} (N-H out-of-plane bending).

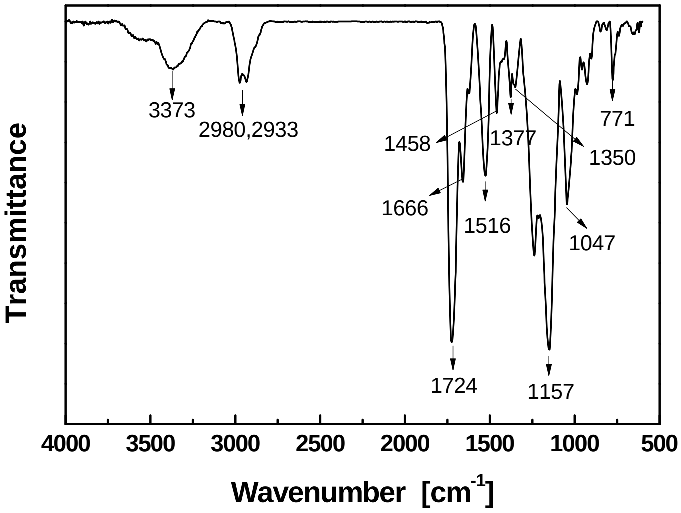


Fig. S9 FTIR spectrum of Dima/PETMP.

FTIR spectrum (KBr) of Dima/PETMP with the following characteristic peaks: 3373 cm^{-1} (-NH stretching), 2980-2933 cm^{-1} (-CH_3 and CH_2 stretching), 1724 cm^{-1} (-C=O of ester and carbamate groups), 1666 cm^{-1} (C=O of amido group), 1516 cm^{-1} (C-N-H bending stretching), 1458 cm^{-1} (-CH_2 bending), 1377 cm^{-1} (-$(CH_3)_2$ anti-symmetric bending), 1350 cm^{-1} (-CH_3 anti-symmetric bending), 1157 cm^{-1} (C-O-C stretching), 1047 cm^{-1} (C-O stretching), and 771 cm^{-1} (N-H out-of-plane bending).

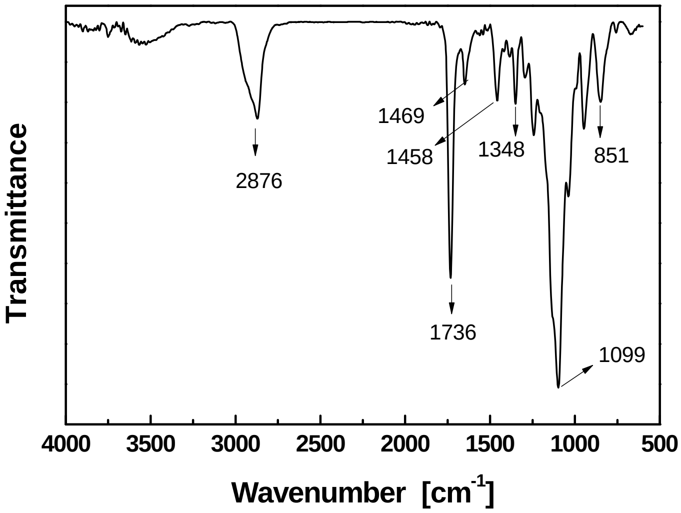


Fig. S10 FTIR spectrum of PEGDMMA/TMPMP.

FTIR spectrum (KBr) of PEGDMMA/TMPMP with the following characteristic peaks: 2876 cm^{-1} (-CH_3 and CH_2 stretching), 1736 cm^{-1} (-C=O stretching), 1469cm^{-1} (-CH_2 connect to ether linkage, symmetric bending), 1458 cm^{-1} (-CH_2, symmetric bending), 1348cm^{-1} (-CH_3, symmetric bending), 1250 cm^{-1} (C-O-C of ester group, symmetric stretching), 1099 cm^{-1} (C-O-C stretching), and 851 cm^{-1} (-$(CH_2)_2$, rocking vibration).

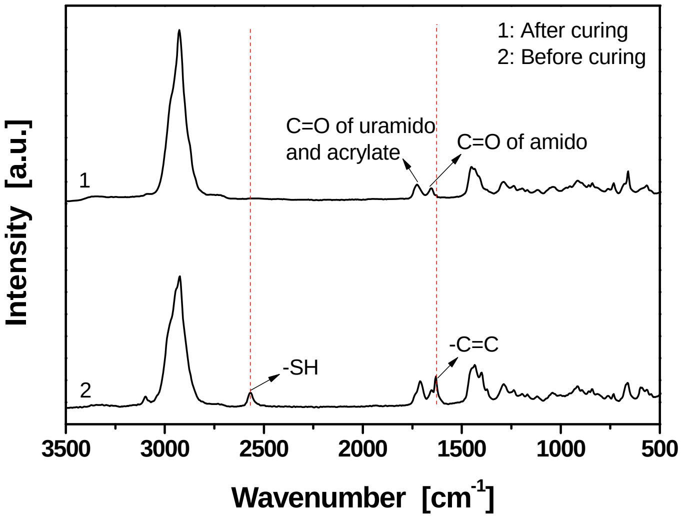


Fig. S11 FT-Raman spectra of Dima/PETMP before and after curing. Before curing, catalyst DBU was absent in the mixture of Dima/PETMP so that no crosslinking reaction took place.

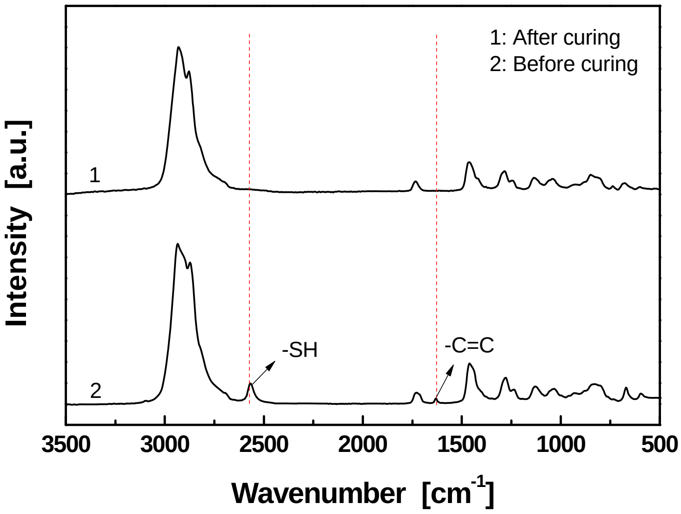


Fig. S12 FT-Raman spectra of PEGDMMA/TMPMP before and after curing. Before curing, catalyst DBU was absent in the mixture of PEGDMMA/TMPMP so that no crosslinking reaction took place.

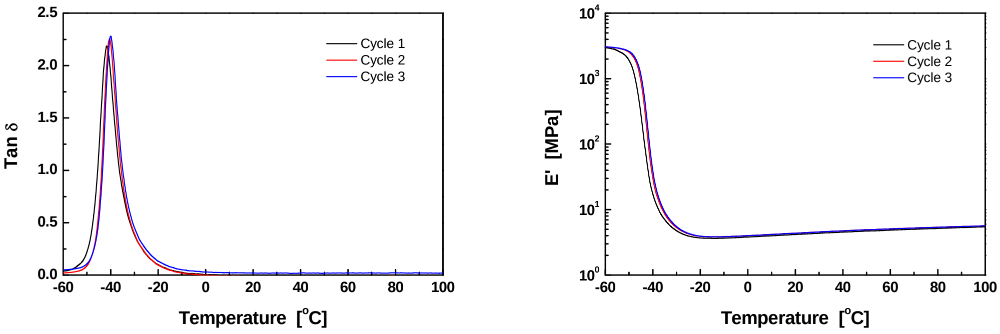
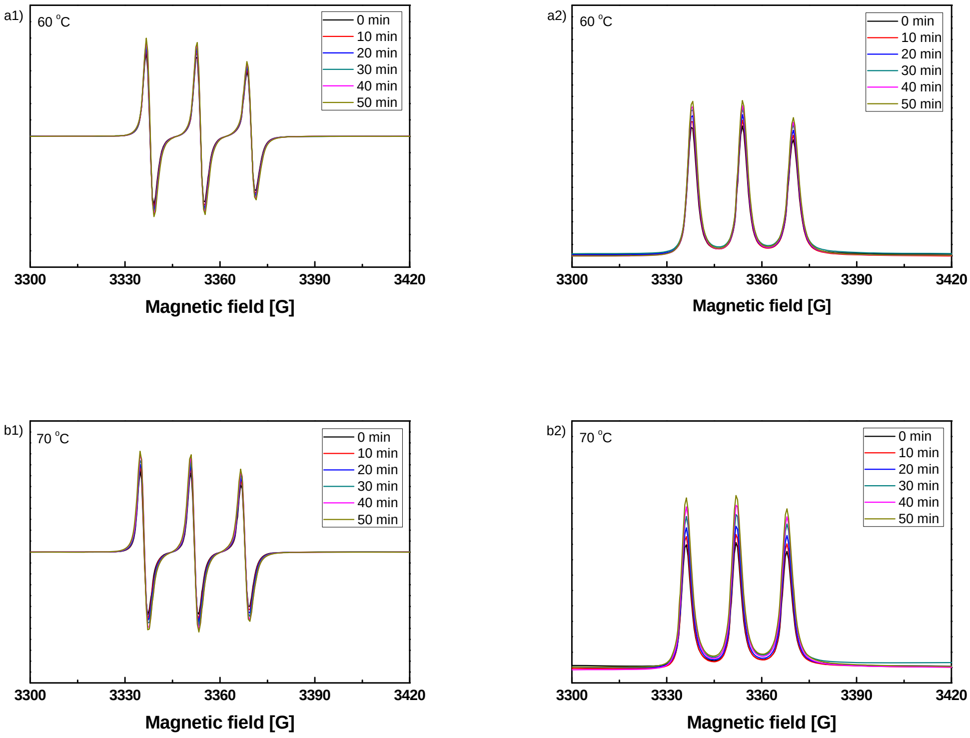


Fig. S13 Temperature dependences of (a) tan *δ* and (b) storage modulus of PEGDMMA/TMPMP measure by repeated DMA scans.



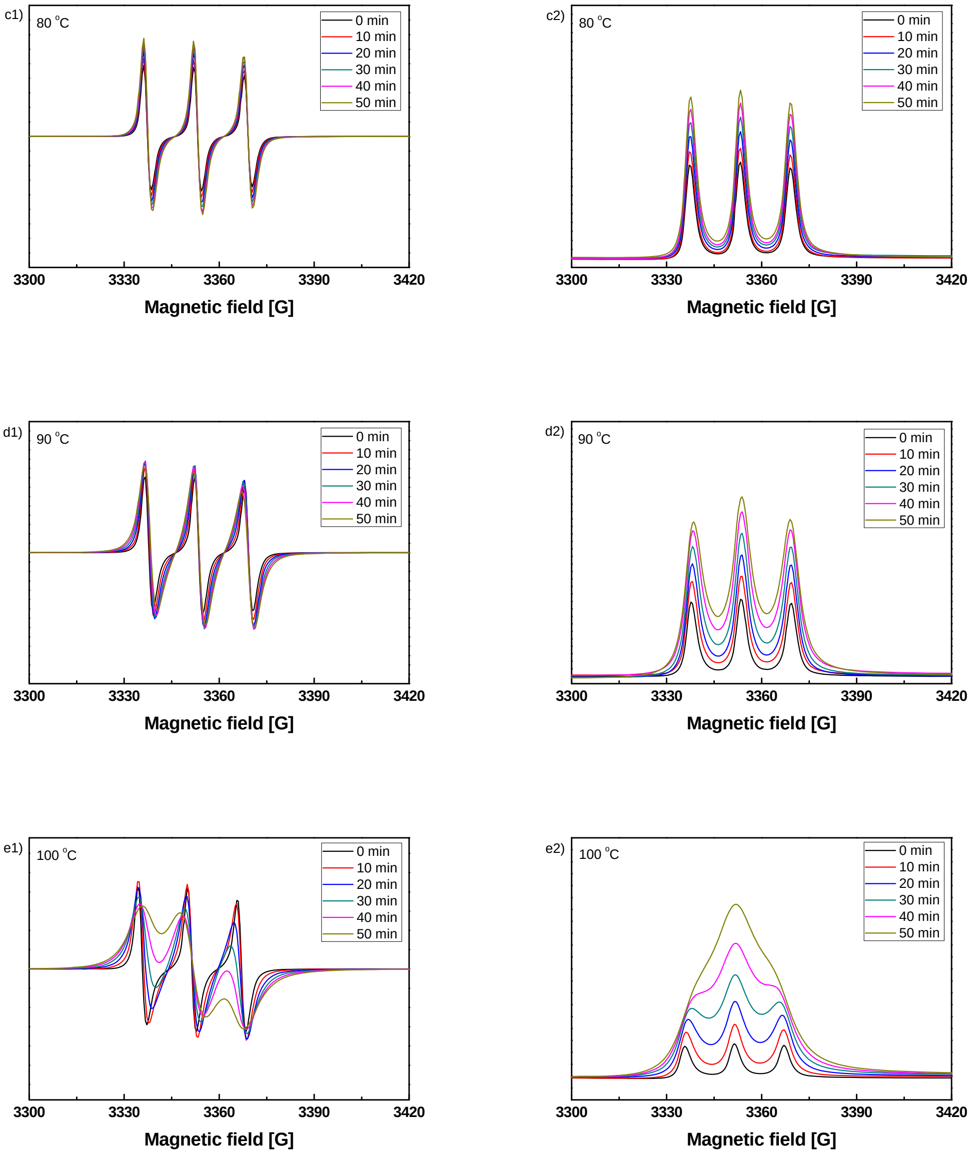


Fig. S14 (a1)-(e1) Effect of heating time on ESR spectra of Diol measured at different temperatures. (a2)-(e2) Normalized absorption lines obtained from the data of (a1)-(e1).