Synthesis of poly(n-butyl methacrylate)-(glycidyl methacrylate) block copolymer and its compatibilization on the interface of QDs/epoxy nanocomposite for white LED encapsulation

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Supporting Information

The copolymerization of BMA with GMA was carried out in molar ratio of 1:1. To explore the suitable reaction conditions for controlled copolymerization, the effect of various reaction parameters i.e. polymerization time, feed order of monomers, polymerization temperature, concentration of reaction solution, molar ratio of monomer and initiator were investigated.

1.1 Effect of polymerization time

Taking the condition (polymerization temperature 50 °C; solvent volume fraction 50 %; PBMA fomed the first block, and PGMA formed the second block; $[CuBr]_0=[EPN-Br]_0=[PMDETA]_0= 0.16$ mol/L, $[BMA]_0= 3.17$ mol/L, $[GMA]_0= 3.17$ mol/L) as an example, the experiment was carried out to confirm whether the polymerization was controllable polymerization.
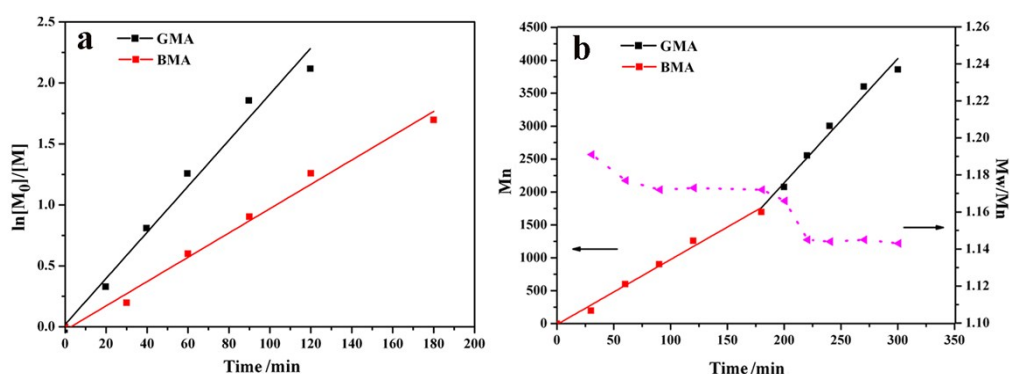

Fig. S1 Variation of $\ln([M_0]/[M])$ (a) and Mn and PDI (b) with reaction time.

(polymerization temperature 50 °C; solvent volume fraction 50 %; PBMA fomed the first block, and PGMA formed the second block; $[CuBr]_0=[EPN-Br]_0=[PMDETA]_0=$ 0.16 mol/L, $[BMA]_0=$ 3.17 mol/L, $[GMA]_0=$ 3.17 mol/L)

As shown in the kinetics plot (Fig. S1a), poly(BMA-b-GMA) copolymer could be synthesized by ATRP, the increases of $\ln([M_0]/[M])$ versus time were linear, and the apparent rate constants were found to be k_{PBMA}=0.59 and k_{PGMA}=1.13 h^{-1}, respectively. Meanwhile, along with the extending of reaction time, the molecular weight of PBMA segment was also in good linear relationship with polymerization time. By controlling polymerization time, the PBMA-Br with expected molecular weight and narrow molecular weight distribution (1.17) could be synthesized as macroinitiator agent. Besides, it also followed the polymerization kinetics characteristics of ATRP when PBMA-Br used as macroinitiator for the polymerization of the PGMA block. PGMA chain segments with controlled molecular weight could be synthesized by controlling the reaction time (Fig. S1b).

1.2 Effect of feed order of monomers

The following experiment was carried out by changing the feed order of monomers and maintaining the other conditions constant (polymerization temperature 50 °C; solvent volume fraction 50 %; PGMA formed the first block, and PBMA formed the second block; $[CuBr]_0=[EPN-Br]_0=[PMDETA]_0=$ 0.16 mol/L; $[BMA]_0=$ 3.17 mol/L, $[GMA]_0=$ 3.17 mol/L).
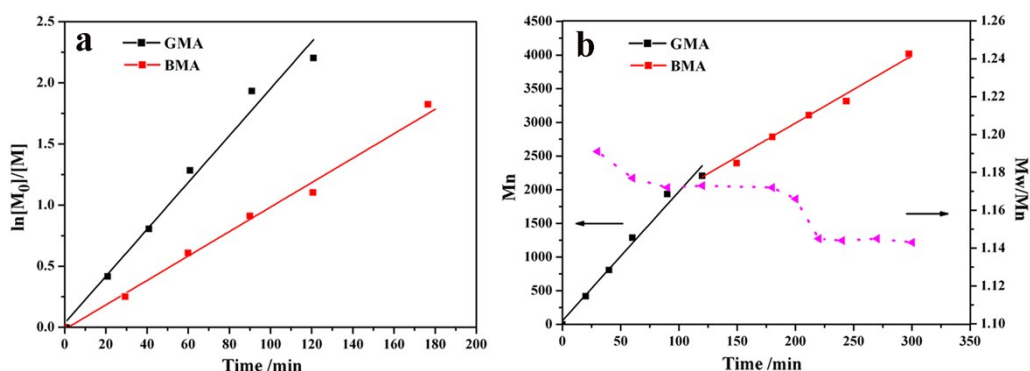
Fig. S2 Variation of $\ln([M_0]/[M])$ (a) and Mn and PDI (b) with reaction time. (polymerization temperature 50 ^{o}C; solvent volume fraction 50 %; PGMA fomed the first block, and PBMA formed the second block; $[CuBr]_0=[EPN\text{-}Br]_0=[PMDETA]_0=$ 0.16 mol/L, $[BMA]_0=$ 3.17 mol/L, $[GMA]_0=$ 3.17 mol/L)

Compared with Fig. S1, for both PGMA and PBMA, the increases of $\ln([M_0]/[M])$ versus time were linear after changing the feed order of monomers, and the apparent rate constants were $k_{PBMA}=0.60$ and $k_{PGMA}=1.15$ h^{-1}, respectively (Fig. S2a). So it could be determined that changing the feed order of monomers caused little impact to PGMA and PBMA polymerization kinetics process, and poly(GMA-b-BMA) block copolymers with controllable molecular weight and narrow molecular weight distribution can also be prepared (Fig. S2b).

1.3 Effect of polymerization temperature

To investigate the effect of temperature, copolymerization was carried out by changing the temperature from 40 to 70 ^{o}C and maintaining the other conditions constant (solvent volume fraction 50 %; PBMA formed the first block, and PGMA formed the second block; $[CuBr]_0=[EPN\text{-}Br]_0=[PMDETA]_0=$ 0.16 mol/L, $[BMA]_0=$ 3.17 mol/L, $[GMA]_0=$ 3.17 mol/L).
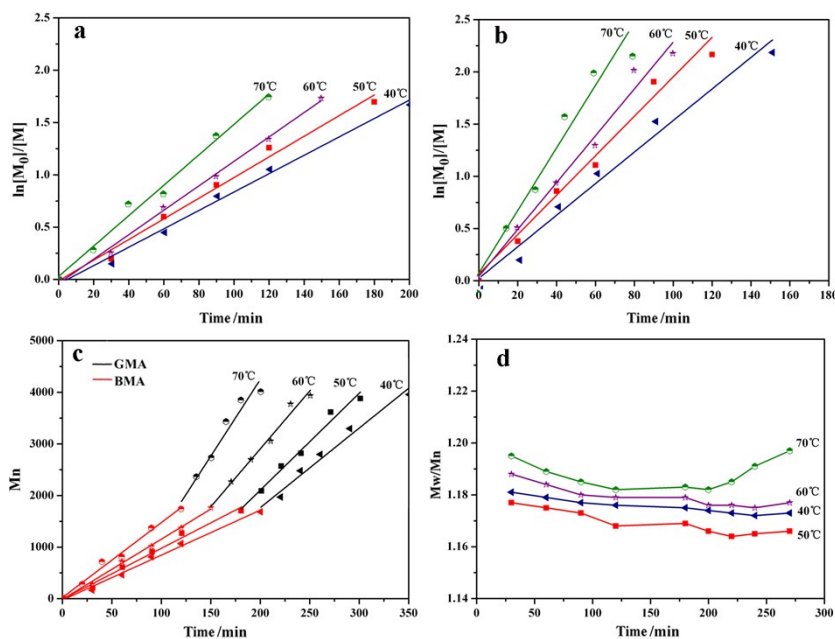
Fig. S3 Variation of $\ln([M_0]/[M])$ with reaction time at different polymerization temperatures (a. PBMA, b. PGMA); Variation of Mn (c) and PDI (d) with reaction time at different polymerization temperatures. (solvent volume fraction 50 %; PBMA fomed the first block, and PGMA formed the second block; $[CuBr]_0 = [EPN-Br]_0 = [PMDETA]_0 = 0.16$ mol/L, $[BMA]_0 = 3.17$ mol/L, $[GMA]_0 = 3.17$ mol/L)

Apparent rate constants of PBMA and PGMA segments appeared increasing trend with the polymerization temperature increased (Fig. S3a, b). For PBMA segment, the k_{PBMA} at 40, 50, 60 and 70 °C was 0.42, 0.59, 0.70 and 0.87 h^{-1}, respectively. Likewise, k_{PGMA} was increased from 0.91 to 1.80 h^{-1} when the polymerization temperature rose from 40 to 70 °C. Calculated according to the Arrehenius equation, polymerization apparent activation energy under this condition were $E_{PBMA}=14.87$, $E_{PGMA}=19.82$ kJ/mol, respectively. Because of the polymerization rate increased, growth rate of PBMA and PGMA each segment molecular weight also increased with the polymerization temperature increased (Fig. S3c). However, the raised reaction temperature increased the activity of the active center, thus weakened the control of molecular weight distribution by polymerization (Fig. S3d). So from the perspective

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of reaction control, the polymerization temperature was chosen as 50°.

1.4 Effect of concentration of reaction solution

To optimize the solvent content effect, copolymerization was performed in solvent content of 30 vol%, 50 vol% and 70 vol%. The other conditions (polymerization temperature 50 °C; PBMA formed the first block, and PGMA formed the second block; $[CuBr]_0=[EPN-Br]_0=[PMDETA]_0=0.16$ mol/L, $[BMA]_0=3.17$ mol/L, $[GMA]_0=$ 3.17 mol/L) maintained constant.
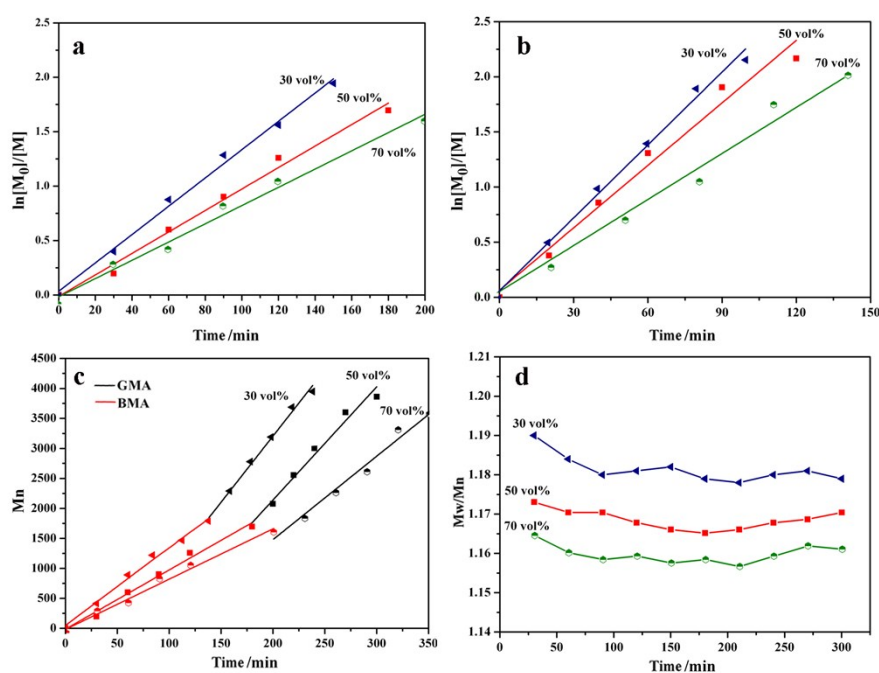

Fig. S4 Variation of ln([M_0]/[M]) with reaction time at different solvent contents (a. PBMA, b. PGMA); Variation of Mn (c) and PDI (d) with reaction time at different solvent contents. (polymerization temperature 50 °C; PBMA fomed the first block, and PGMA formed the second block; $[CuBr]_0=[EPN-Br]_0=[PMDETA]_0=0.16$ mol/L, $[BMA]_0=3.17$ mol/L, $[GMA]_0=3.17$ mol/L)

The increase of solvent content reduced the collision probability of monomer and active center, and the apparent rate constants of PBMA and PGMA were decreased (Fig. S4a, b). For PBMA, when the solvent content was 30, 50 and 70 vol%, the

k_{PBMA} was 0.78, 0.59, and 0.42 h^{-1}, respectively. Likewise, k_{PGMA} was decreased from 1.32 to 0.83 h^{-1} when the solvent content increased from 30 to 70 vol%. Therefore, growth rate of PBMA and PGMA each segment molecular weight decreased (Fig. S4c) and molecular weight distribution reduced with the solvent content increased (Fig. S4d). So the solvent content was chosen as 50 vol% in order to obtain block copolymer with desired molecular weight.

1.5 Effect of molar ratio of monomer and initiator

All the following three groups of experiments were done by changing the molar ratios of monomer and initiator (50:1, 20:1 and 10:1) and maintaining the other conditions constant (polymerization temperature 50 °C; solvent volume fraction 50 %; PBMA formed the first block, and PGMA formed the second block; $[BMA]_0$= 3.17 mol/L, $[GMA]_0$= 3.17 mol/L).
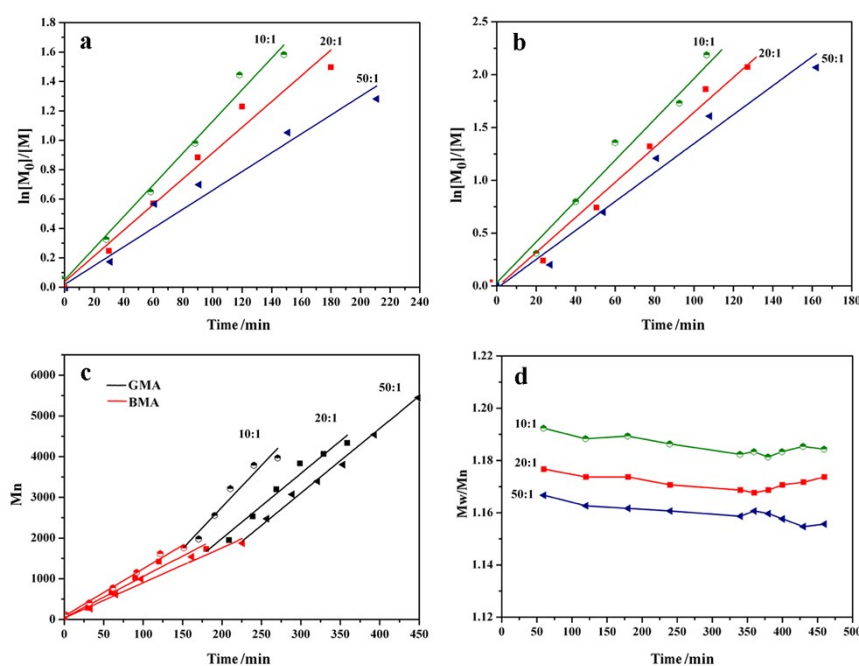

Fig. S5 Variation of ln($[M_0]$/[M]) with reaction time at different molar ratios of monomer and initiator (a. PBMA, b. PGMA); Variation of Mn (c) and PDI (d) with reaction time at different molar ratios of monomer and initiator. (polymerization

temperature 50 $^{\circ}$C; solvent volume fraction 50 %; PBMA fomed the first block, and PGMA formed the second block; $[BMA]_0= 3.17$ mol/L, $[GMA]_0= 3.17$ mol/L)

The increase of initiator content increased the number of active center, and then improved the collision probability of monomer and active center, thus the apparent rate constants of PBMA and PGMA were increased (Fig. S5a, b). For PBMA, when the molar ratio of monomer and initiator was 50:1, 20:1 and 10:1, the k_{PBMA} was 0.38, 0.59, and 0.65h^{-1}, respectively. Likewise, k_{PGMA} was increased from 0.89 to 1.28h^{-1} when the molar ratio of monomer and initiator changed from 50:1 to 10:1. The increase of reaction rate made the growth rate of PBMA and PGMA each segment molecular weight increased (Fig. S5c), but the molecular weight distribution became wider (Fig. S5d). Considering polymerization rate and required molecular weight of the copolymer, the molar ratio of monomer and initiator was chosen as 20:1.

In conclusion, the experiment conditions in preparation of a template for the ligand were chosen as follows: PBMA fomed the first block, and PGMA formed the second block; polymerization temperature 50 $^{\circ}$C; solvent volume fraction 50 %; the molar ratio of monomer and initiator 20:1. Through controlling polymerization time, copolymers with desired molecular weight were obtained for modification of QDs.