






Cite this: *Polym. Chem.*, 2021, **12**, 6606

Highly branched polymethacrylates prepared efficiently: brancher-directed topology and application performance†

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Highly branched polymers are very promising and suitable for a variety of applications. Herein, a series of oil-soluble and branched polymethacrylates are synthesized efficiently *via* atom transfer radical copolymerization of 2-ethylhexyl methacrylate (EHMA) with different divinyl branchers. More remarkably, for the first time, it is found that the brancher significantly affects not only the branching degree, but also the branch structure, thus determining the application performance of the branched polymethacrylates. The order of branching degree from high to low with the brancher is *p*-divinylbenzene (DVB) > ethylene glycol dimethacrylate > *p*-vinylbenzyl methacrylate. In addition, only the brancher DVB provides branched polymers with negligible linear components, further indicating that DVB is the most effective brancher. More interestingly, it is deduced that the brancher DVB produces branched polymers possessing "X"-like branch-linkages, while the other two branchers provide "T"-like linkages. These brancher effects could be well explained by the reactivity ratios of the different double bonds in the polymerization system. The polymethacrylates with "X"-like branch-linkages exhibit superiority in comprehensive performance as viscosity index improvers (VIIs) of lubricants compared to those with "T"-like linkages and linear polymers, including a commercial analogue. Among the branched polymers of EHMA, the EHMA/DVB copolymer achieves the best VI improving power and viscosity thickening capacity. More notably, this sample exhibits a unique performance of shear thickening and a negative shear stability index, which make it ideal for the potential applications as an additive of premium lubricants involving high shear stress.

Received 22nd September 2021,
Accepted 31st October 2021

DOI: 10.1039/d1py01273h

rsc.li/polymers

Introduction

Highly branched polymers have become a very promising type of polymer because of their divergent three-dimensional globular structure and the large number of terminal functionalities.^{1–4} They are suitable candidates for a variety of applications, from biomaterials and drug delivery systems⁵ to more applied fields such as wastewater treatment,⁶ coatings,⁷ inkjet printing,⁸ encapsulation technologies,⁹ and lubricant additives (such as viscosity index improvers (VIIs)).¹⁰ The synthesis of branched polymers can be achieved by the classical

polycondensation of AB_n-type monomers,^{11,12} the self-condensing vinyl polymerization of inimers,^{13,14} the controlled radical homopolymerization of divinyl monomers,^{2,15} or the copolymerization of a vinyl monomer with a small amount of divinyl or multivinyl brancher (Strathclyde route).^{16–19} The last route is attractive, as it can be carried out using cheap, readily available monomers and branchers to synthesize branched polymers with abundant structures and various molecular weight (MW) levels, and holds good promise in terms of large-scale production.

Conventional free radical polymerization (FRP) can be used for the synthesis of highly branched polymers *via* the Strathclyde route. However, this method usually leads to gelation even at the very early stages of polymerization because of its intrinsic limitations of slow initiation rates and fast chain propagation and termination reactions.²⁰ Numerous efforts have been devoted to preventing gelation, such as using a large amount of chain transfer agent^{18,21–26} or employing controlled radical polymerizations.^{27–30} Among these strategies, atom transfer radical copolymerization (ATRCp) has received extensive attention, as its pseudo-living character offers a

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†Electronic supplementary information (ESI) available. See DOI: 10.1039/d1py01273h

number of advantages for the synthesis of branched polymers *via* the Strathclyde route, such as the readily controlled primary chain length and the relatively low dispersity. This means that the probability of unwanted macrogelation due to cross-linking caused by a minor population of longer chains is significantly reduced. Besides, in a copolymerization system of a monovinyl monomer with a small amount of a divinyl cross-linker or brancher reported by Matyjaszewski and Armes, respectively, the experimental result combined with theoretical simulation proved that the ATRP technology resulted in very low levels of intramolecular cyclization and a more homogeneous crosslinked or branched structures compared with the FRP process.^{31,32}

Several research groups systematically studied the synthesis of branched polymers and/or gels *via* the ATRcP of monovinyl monomers and divinyl branchers.^{31–35} However, to date, most of these studies are based on the copolymerization of (methyl) methacrylate,³⁰ styrene^{36,37} or 2-hydroxypropyl methacrylate.^{38,39} Besides, highly branched polymers obtained by this route generally inevitably contain considerable linear components.^{14,30} Furthermore, the effects of divinyl branchers or crosslinkers are rarely discussed in all these studies. Matyjaszewski's studies elucidated the effect of cross-linker reactivity on the spatial distribution of pendant vinyl groups and the experimental gel points.^{34,35} Sherrington investigated the differing behaviors of the divinyl branchers using conventional free radical copolymerization of MMA in the presence of a chain transfer agent, showing that a divinyl benzene mixture produced the more regularly branched material with narrower molar mass distribution than ethylene glycol dimethacrylate (EGDMA) and ethylene glycol diacrylate.¹⁸ A very good work reported by Jiang *et al.*³⁶ demonstrates the significant brancher effect on the polymer branching structure in the ATRcP of styrene with different branching agents, which is mainly attributed to the different polar interactions between styrene and the divinyl brancher. They clarified that polymers prepared using 1,6-bismaleimido-hexane (BMIH) as the branching agent contained not only star-like but also randomly branched molecules, while polymers prepared using either tri-EGDMA or DVB as the brancher have similar randomly branched structures. To the best of our knowledge, to date, there has been no report specially on the synthesis of highly oil-soluble and branched polymethacrylates *via* the ATRcP of monovinyl monomers and divinyl branchers. The brancher effect on the branching degree and the branch structure of polymethacrylates has not attracted enough attention, not to mention the effect on the application properties of the branched polymers. Thus, it is of considerable interest to evaluate the use of ATRcP in the synthesis of highly oil-soluble and branched polymethacrylates with negligible linear components. Furthermore, it is definitely important to establish correlations between the brancher reactivity and polymer structure, and between the polymer structure and properties.

In this work, we focus on the effect of the divinyl brancher employed in ATRcP reaction on the topology and the application performance as a VII of branched polymethacrylates.

Highly oil-soluble and branched polymethacrylates have been synthesized with nearly complete conversion and negligible linear components, employing our bisoxazoline/copper catalyst (Fig. 1a).^{40–45} More remarkably, for the first time, it is found that the brancher significantly affects not only the branching degree but also the branch structure (Fig. 1), thus determining the application performance of the branched polymethacrylates. These brancher effects well correspond to the reactivity ratios of the different double bonds in the polymerization system. By engineering the polymer topology *via* simply selecting an easily available divinyl brancher, it is very convenient to prepare various branched polymethacrylates, which prove to be potential VIIs with unique and excellent performance.

Results

Synthesis and structure identification of highly branched polymethacrylates

Firstly, we conducted the supplemental activation and reducing agent (SARA) ATRcP of EHMA with EGDMA at ambient temperature employing our bisoxazoline/copper catalyst at $[\text{EHMA}]_0/[\text{EGDMA}]_0/[\text{initiator}]_0 = 50/1/1$, in which 2-bromopropionitrile (BPN) and THF/DMSO are used as the initiator and mixed solvent, respectively (Table 1). According to the Flory–Stockmayer theory, in order to avoid gelation, the numbers of branching sites per primary chain should not exceed unity.^{30–35,38,39} The molecular weight ($M_{n,RI}$) of the EHMA homopolymer obtained under the same conditions indicates that the initiation efficiency of the polymerization is about 90%. On the other hand, a small amount of EGDMA units cannot generate branches due to cyclization reaction or retaining pendant vinyl groups. Therefore, one equivalent of the divinyl brancher to initiator is used. Fig. 2a shows that during the polymerization with a $\text{conv.}_{\text{EHMA}}$ lower than 95%, the first-order kinetic plot of EHMA is linear. It can be estimated that the radical concentration is constant in the reaction system, as the content of EHMA is much higher than that of the divinyl brancher.^{19,38} The conversion of EGDMA is always higher than that of EHMA which might be due to the presence of two reactive vinyl bonds in EGDMA. As shown in Fig. 2b, where the brancher is present, M_n increases more or less linearly up to about 95% conversion, closely resembling the linear regression for the homopolymerization of EHMA and indicating a “living” nature of the ATRcP system and negligible side reactions of radical termination. A steep increase of M_n and dispersity values (M_w/M_n) occurs in the last 5% conversion during the copolymerization of EHMA in the presence of a brancher, which is different from the case of EHMA homopolymerization and suggests the generation of branched structures.^{19,37} Fig. 3 shows the evolution of the differential molecular weight distribution of PEHMA₅₀-EGDMA_{1.0} with reaction time obtained with a refractive index (RI) detector. At low conversions, the distribution curves are monomodal. At around 95% conversion (20 h), there is clear evidence that multiples of the primary chains form, confirming the generation of branched

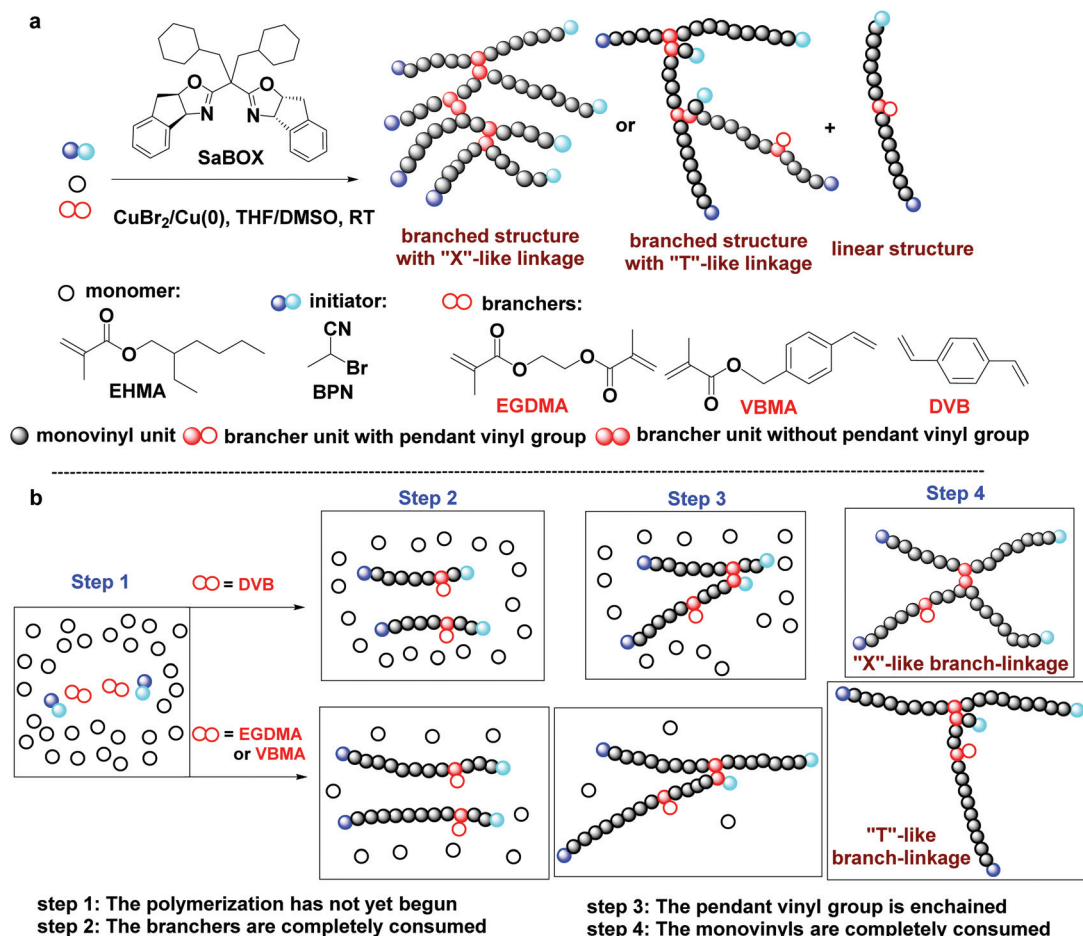


Fig. 1 (a) ATRCp for the synthesis of branched polymethacrylates. (b) The proposed process of forming "X"-like and "T"-like branch-linkages by using different branchers inferred from the results of tracking molecular weight during the polymerization process.

Table 1 Summary of linear and branched polymers prepared with various branchers^a

Polymer	$M_{n,RI}$ (kg mol^{-1})	$M_{w,RI}$ (kg mol^{-1})	D_{RI}	$M_{n,LS}$ (kg mol^{-1})	$M_{w,LS}$ (kg mol^{-1})	D_{LS}	Residual ^b C=C (%)	Branching coefficient ^c	α^d
PEHMA ₅₀	10.6	13.7	1.3	14.0	18.1	1.3	—	—	—
PEHMA ₅₀ -EGDMA _{1.0}	21.4	64.2	3.0	30.2	104.1	3.4	18	0.50	0.35
PEHMA ₅₀ -DVB _{0.75}	34.9	99.2	2.8	55.2	182.5	3.3	0	0.70	0.45
PEHMA ₅₀ -VBMA _{1.0}	15.1	22.8	1.5	25.8	36.4	1.4	44	0.30	0.39
PEHMA ₆₀₀	106.4	169.4	1.6	163.7	234.5	1.4	—	—	0.61

^a Reaction conditions: $[\text{CuBr}_2]/[\text{Cu}]/[\text{SaBOX}]/[\text{EHMA}]/[\text{divinyl brancher}]/[\text{BPN}] = 1/4/2/100/x/2$ ($x = 2$ for EGDMA and VBMA, 1.5 for DVB), THF/DMSO (v/v = 7/1) as the solvent, $[\text{EHMA}]_0 = 1.7 \text{ M}$, $V_{\text{total}} = 28.2 \text{ mL}$, $30 \text{ }^\circ\text{C}$, 72 h, and conv. (EHMA) > 99%. Tracing is carried out. ^b The ratio of residual double bonds in the brancher units, measured by ¹H NMR (for detailed analysis and calculation methods, see the ESI[†]). ^c The closer it is to 1, the higher the branching degree, calculated based on eqn (1). ^d Mark-Houwink parameter determined with a viscosity detector.

polymers with high molecular weight and broad MW distribution.^{18,46}

The branching coefficient is calculated as 0.50, according to eqn (1), where $M_{n,b}$ and $M_{n,l}$ are respectively the molecular weights of the branched polymer and the linear polymer produced under the same conditions in the absence of a brancher.³⁶ It is believed that the RI system underestimates the true molecular weights significantly as a result of the 3-dimen-

sional shape of the polymers synthesized.^{19,37,47} As shown in Table 1, the measured multiangle light scattering (LS) molecular weight ($M_{n,LS} = 30.2 \text{ kg mol}^{-1}$, $M_{w,LS} = 104.1 \text{ kg mol}^{-1}$) is much higher than the RI result ($M_{n,RI} = 21.4 \text{ kg mol}^{-1}$, $M_{w,RI} = 64.2 \text{ kg mol}^{-1}$), strongly supporting the formation of a highly branched architecture.⁴⁸ The intrinsic viscosity ($[\eta]$) plot of PEHMA₅₀-EGDMA_{1.0} in Fig. 4 is below that of linear PEHMA₆₀₀. The Mark-Houwink parameter (α) for PEHMA₅₀-

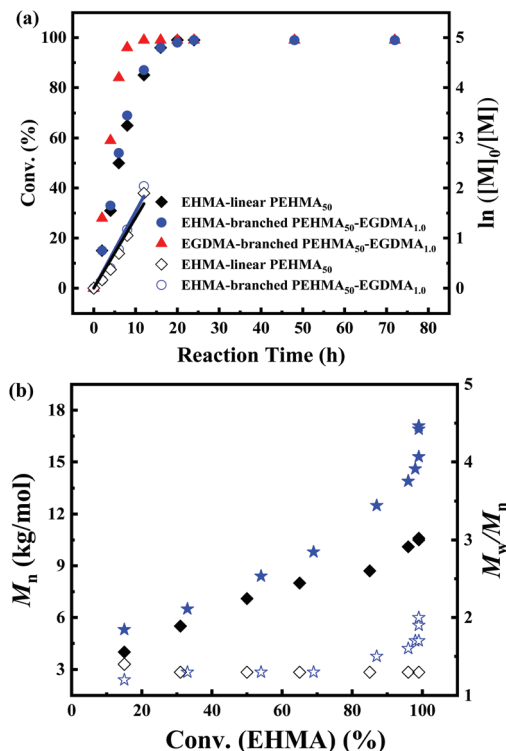


Fig. 2 ATRP kinetic data for the synthesis of PEHMA₅₀ and PEHMA₅₀-EGDMA_{1.0}. (a) Conversion (filled points) and $\ln([M]_0/[M])$ (unfilled points) versus time for EHMA (blue) and EGDMA (red) during the synthesis of the branched copolymer PEHMA₅₀-EGDMA_{1.0} as well as for EHMA during the synthesis of linear PEHMA₅₀ (black). (b) M_n (filled points) and M_w/M_n (unfilled points) versus conversion during the synthesis of PEHMA₅₀-EGDMA_{1.0} (blue) and PEHMA₅₀ (black).

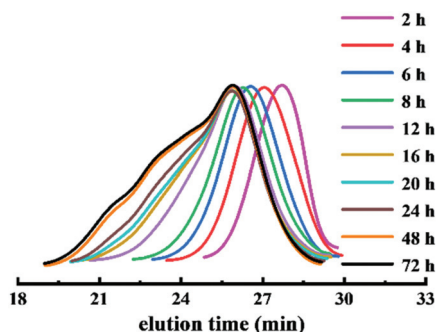


Fig. 3 The evolution of the differential molecular weight distribution with reaction time obtained with the RI detector.

EGDMA_{1.0} is 0.35 (Table S1[†]), which is substantially lower than that of the linear polymer (0.61). These results also confirm the highly branched structure of the resultant PEHMA₅₀-EGDMA_{1.0}.⁴⁹ As shown in the ¹H NMR spectrum of the isolated PEHMA₅₀-EGDMA_{1.0}, the signals at 6.16 and 5.44 ppm are attributed to the pendant methacrylic protons in the EGDMA units (Fig. S1[†]). A comparison of the corresponding signal integrals of the copolymerization mixture reveals that 18% of EGDMA units contain pendant vinyl

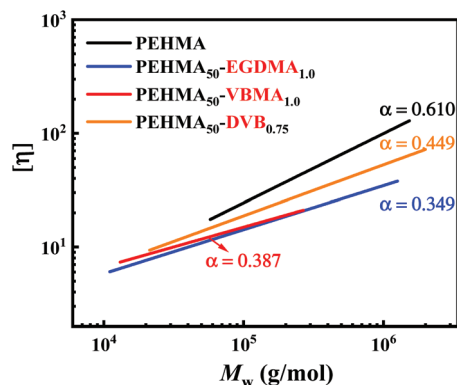


Fig. 4 Intrinsic viscosity ($[\eta]$) for PEHMA₆₀₀, PEHMA₅₀-EGDMA_{1.0}, PEHMA₅₀-DVB_{0.75}, and PEHMA₅₀-VBMA_{1.0}.

groups (for detailed analysis and calculation methods, see the ESI[†]).

$$\text{Branching coefficient} = (M_{n,b} - M_{n,l})/M_{n,b} \quad (1)$$

Brancher effect

Subsequently, the brancher effect on the polymerization process and copolymer structure is studied in detail under similar conditions ($[EHMA]_0/[brancher]_0/[BPN]_0 = 50/1$ or $0.75/1$). The branchers include EGDMA, *p*-divinylbenzene (DVB) and *p*-vinylbenzyl methacrylate (VBMA). The results show that all the monomers and branchers achieve a nearly complete conversion (>99%). When DVB was examined as the brancher under the same conditions as the EGDMA system ($[EHMA]_0/[brancher]_0/[BPN]_0 = 50/1/1$), the copolymer PEHMA₅₀-DVB_{1.0} could not be prepared as a soluble and branched, rather than a gelled product. This result might have been obtained mainly because it is much easier for the styrene moiety of the DVB unit to be incorporated into the EHMA polymer chain compared to the methacrylate moiety of EGDMA units. Besides, on steric grounds, the DVB unit might have a less propensity towards cyclization than the EGDMA unit.^{36,38} Therefore, DVB is more promising as a brancher. Next, the copolymerization at a lower brancher loading ($[EHMA]_0/[DVB]_0/[BPN]_0 = 50/0.75/1$) was conducted and it provided a completely soluble copolymer (PEHMA₅₀-DVB_{0.75}). Notably, the ¹H NMR spectrum of PEHMA₅₀-DVB_{0.75} indicates the complete absence of any signals due to pendant unreacted vinyl groups (Fig. S2[†]). Overall, the branching process involving DVB seems to be a smoother, more regular process in the sense that both of the DVB vinyl groups seem to be used efficiently in generating branches. When the nonsymmetrical VBMA was employed as the brancher ($[EHMA]_0/[VBMA]_0/[BPN]_0 = 50/1/1$), the result showed that the remaining pendant double bonds of VBMA units in the copolymer PEHMA₅₀-VBMA_{1.0} were all on the methacrylate side with a high content of 44% (for detailed analysis and calculation methods, see the ESI[†]), suggesting a low branching degree (Fig. S3[†]). This result further demonstrates the preference of the styrene moiety for inserting into the EHMA polymer chain compared with the methacrylate moiety.

The $M_{n,RI}$ data for the copolymers PEHMA₅₀-DVB_{1.0}, PEHMA₅₀-EGDMA_{1.0} and PEHMA₅₀-VBMA_{1.0} are 34.9, 21.4, and 15.1 kg mol⁻¹, respectively, while the $M_{n,LS}$ data are 55.2, 30.2, and 25.8 kg mol⁻¹. (Table 1). The branching coefficients for these three polymers are 0.70, 0.50 and 0.30, respectively. It is clear that the copolymer PEHMA₅₀-DVB_{0.75} has the highest number-average molecular weight, the greatest difference in RI and LS number-average molecular weight data and the highest branching coefficient. All these results indicate that the order of branching degree for these three copolymers is PEHMA₅₀-DVB_{0.75} > PEHMA₅₀-EGDMA_{1.0} > PEHMA₅₀-VBMA_{1.0}.

As mentioned above (Fig. 2b), during the synthesis of the branched polymer, M_n increases linearly with conversion before generating branches, closely resembling the linear regression for the homopolymerization of EHMA. Therefore, if some primary chains fail to combine with others *via* inter-macromolecular radical addition, the branched polymer will contain a significant amount of linear structure and its GPC elution curve should overlap with that of linear PEHMA₅₀ obtained under similar conditions.^{19,35,37} Remarkably, as shown in Fig. 5, when VBMA is used as the brancher, the RI curve of the resultant PEHMA₅₀-VBMA_{1.0} mostly overlaps with that of linear PEHMA₅₀ obtained in the absence of a brancher, indicating that PEHMA₅₀-VBMA_{1.0} is dominated by a linear or near-linear structure. Similarly, when EGDMA is used as the brancher, a significant portion of the RI curve of the branched products overlaps with those of linear polymers, suggesting that the products contain considerable linear or near-linear components. In contrast, when the brancher DVB is employed, the GPC-RI curve of the obtained polymer has slight overlap with that of the linear polymer. The multipeak splitting using the Gaussian function could not distinguish the linear components,¹⁹ indicating that the linear structure is negligible. These results further demonstrate that DVB is the most effective brancher.

More importantly, it is deduced that the brancher not only leads to great differences in the molecular weight, branching degree and components of the polymer, but also seriously affects the branch structure of the polymer. As shown in Fig. 6, when EGDMA, VBMA and DVB are employed as the branchers,

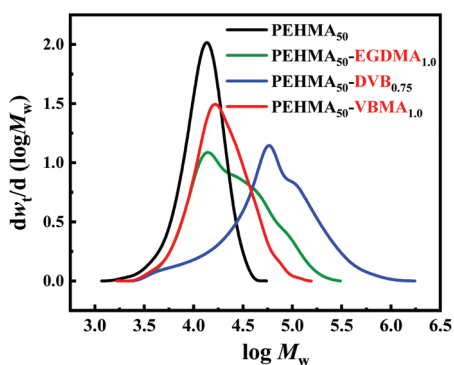


Fig. 5 RI curves: PEHMA₅₀, PEHMA₅₀-VBMA_{1.0}, PEHMA₅₀-DVB_{0.75} and PEHMA₅₀-EGDMA_{1.0}.

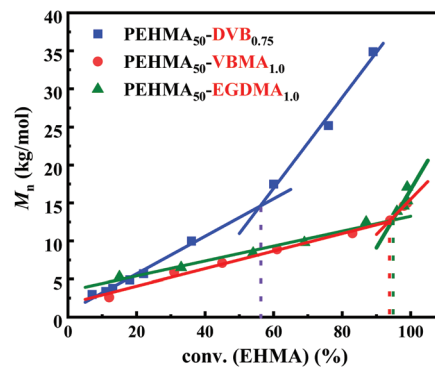


Fig. 6 The curves showing M_n versus conversion obtained with the RI detector for the synthesis of PEHMA₅₀-DVB_{0.75}, PEHMA₅₀-EGDMA_{1.0} and PEHMA₅₀-VBMA_{1.0}.

a steep increase of MW occurs at EHMA conversions of 96%, 94% and 56%, respectively, and meanwhile, the MW distributions rapidly widen (Fig. 2b and Fig. S4†). The sharp rise in molecular weight and the dispersity value is generally caused by large-scale inter-macromolecular addition reactions of a macromolecule radical with a pendant double bond introduced by a divinyl brancher.^{19,37,38} Thus, when EGDMA and VBMA are used as the branchers, EHMA is nearly completely consumed before the hanging double bonds are incorporated into another primal chain. After that, the branched chain nearly stops propagating. The length ratios of two branched chains generated by a brancher are about 24/1 and 16/1 when using EGDMA and VBMA, respectively, forming a local structure with a “T”-like branch-linkage (Fig. 1b). In contrast, when DVB is used as the brancher, about 44% of the monomers remain when the pendant double bonds participate in the polymerization to form branched chains. The branched chain could continue growing to about twice the original length and the length ratio of two branches generated by one DVB unit is about 1/1, forming a local structure with an “X”-like branch-linkage (Fig. 1b). Therefore, compared with the other two branchers, when DVB is used, more branched chains are produced by each branching site and the branched chains are relatively short. As for the EGDMA or VBMA system, if the monomer is supplemented after the complete conversion, the “T”-like linkage will transform into an “X”-like linkage. It should be noted that, similar to the method used by Matyjaszewski,⁵⁰ the models of “T”-like and “X”-like branch-linkages are proposed to clearly illustrate the whole branching process, and are inferred from the results of tracking molecular weight during the polymerization process. They do not refer to the structure of the whole polymer chain, but the local structure centered at a branching point, and thus direct evidence, such as images, is difficult to provide. The intrinsic viscosity plots of these polymers also support the difference in their topological structures. As shown in Fig. 4, the polymers with EGDMA and VBMA as branchers have very similar α and $[\eta]$ at the same molecular weight, while the polymer with DVB as the branching agent has a relatively high α value and viscosity. α and $[\eta]$

values are influenced by many factors, such as the functionality and concentration of the multifunctional monomer, the structure and degree of branching, as well as the concentration of the polymer solution.^{17,51} Both α and $[\eta]$ values are generally negatively correlated with the branching degree and/or the length of the branched chain.^{4,52–54} The higher α and $[\eta]$ of PEHMA₅₀-DVB_{0.75} indicate that longer branched chains contribute more to the reduction of polymer viscosity and α value compared to more branched chains for this branched polymer series. These differences in topology and viscosity indicate that the branched polymers obtained using different branchers will exhibit varying performances as the VII of the lubricant.

Performance as a viscosity index improver

A viscosity index improver is indispensable for the formulation and performance design of multigrade engine oils, hydraulic fluids, and transmission fluids. The fuel efficiency of an engine is highly dependent on the ability of a polymer with a high viscosity index (VI) value to provide a minimal thickening at low temperatures, while preventing the fluid from thinning at elevated temperatures. Shear stability is also very important for VIIs, as high-shear conditions are ubiquitous in most mechanical systems.⁵⁵ A linear polymer of high molecular weight may provide a high VI; however, it suffers tremendously from a dramatic molecular weight decrease caused by irreversible chain breakage under the high mechanical shear conditions (poor shear stability).^{56–59} Therefore, even the polymers with excellent VI performance can lose their efficacy only after a few engine run cycles reducing the efficiency and life cycle of the lubricant. It is a conventional belief that highly branched polymers exhibit much higher shear stabilities at high molecular weights due to their compact globular structures compared to linear polymers with similar molecular weights and compositions.^{60,61}

Then the three types of highly branched polymethacrylates produced using EHMA as the main monomer and DVB, EGDMA and VBMA as the branchers, respectively, were evaluated as VIIs with respect to their VI improving ability and shear stability performance (Table S1 and Fig. S5†). The absolute weight-average molecular weight of linear PEHMA₅₀ ($M_{w,LS} = 18.1 \text{ kg mol}^{-1}$) is far lower than those of branched polymers, so it is unfair to compare its performance as a VII with that of branched polymers. Therefore, the linear polymer PEHMA₆₀₀ (Table 1), with a molecular weight ($M_{w,LS} = 234.5 \text{ kg mol}^{-1}$) comparable to those of branched polymers, was synthesized and also used as a potential VII. For a comparison purpose, the performance of a commercial VII based on a linear polymethacrylate (TK-chem V6545) was also tested. The linear and branched polymethacrylates were blended into the 150 N base oil^{56,62–64} (for more information on the 150 N base oil, see the ESI†) to prepare formulated lubricants. Two polymer concentration levels at weight percentages of 1 wt% and 5 wt% in the formulated lubricants were applied. All the polymers show good solubility in the base oil at 1 wt% concentration. When the loading was increased to 5 wt%, only the lubricants formulated with PEHMA₅₀-DVB_{0.75} and PEHMA₅₀-VBMA_{1.0} showed a

clear appearance. As shown in Fig. S5a,† the addition of 5 wt% of linear PEHMA₆₀₀ affords the formulated lubricant with a hazy appearance (IV), while the addition of 5 wt% of branched PEHMA₅₀-DVB_{0.75} still affords the highly transparent formulated lubricant (II), which is consistent with the results of the transmittance test (Table S1†). These results demonstrate the solubility advantage of branched polymers over linear polymers with similar molecular weights. The solubility of the VII influences not only the appearance but also the performance stability of the lubricant.^{65–68} Besides the polymers, no other additives were used in the lubricant formulations.

ΔVI and $\Delta KV100$ refer to the variations in the viscosity index (VI) and kinematic viscosity of the lubricant at 100 °C (KV100) after adding the polymer VII, respectively, which are commonly used to assess the VI improving power and viscosity thickening capacity of the polymer VII. As shown in Fig. S5b and S5c,† compared with the branched polymers obtained using other branchers, PEHMA₅₀-DVB_{0.75} exhibits a better viscosity thickening ability and VI improving capacity, with higher ΔVI and $\Delta KV100$ values, regardless of the concentration of 1 wt% or 5 wt%. Generally, the polymer ability of viscosity thickening and VI improving usually enhances with a change of the chain topology from a highly branched to a linear structure.^{56,58,59} Linear PEHMA₆₀₀ excels in viscosity thickening capacity. However, despite its high molecular weight, PEHMA₆₀₀ does not show obvious superiority in improving the VI value (Fig. S5b†), compared with branched PEHMA₅₀-DVB_{0.75}, especially at 1 wt% concentration ($\Delta VI = 22$ versus 21). Although the VI value obtained with PEHMA₆₀₀ is higher than that with branched PEHMA₅₀-DVB_{0.75} at 5 wt% concentration ($\Delta VI = 69$ versus 57), this difference is not very large and might be mainly due to the difference of molecular weight rather than of topology, as the VI achieved by linear polymers is usually >40 higher than that of branched polymers with similar molecular weights at 5 wt% concentration in the literature reports.^{56,58} Notably, commercial TK-chem V6545 performs inferiorly, with respect to the viscosity thickening ability and VI improving power, compared to branched PEHMA₅₀-DVB_{0.75}.

To examine the effect of the chain topology on the shear stability of the polymers, the Kurt Orbahn (KO) test (for details, see the ESI†), which is commonly used for the shear stability testing of VIIs, was conducted on these lubricant samples.^{56–59} Two commonly used parameters, the percentage kinematic viscosity loss (KV100 loss (%), eqn (2)) and shear stability index (SSI, eqn (3)), are used to quantify the macromolecular shear degradation. The smaller they are, the higher the shear stability is. η_f is the kinematic viscosity of the fresh unshared lubricant, η_s is the kinematic viscosity of the sheared lubricant and η_0 is the kinematic viscosity of the base oil at 100 °C.

$$KV100 \text{ loss } (\%) = (\eta_f - \eta_s) / \eta_f \times 100 \quad (2)$$

$$SSI = (\eta_f - \eta_s) / (\eta_f - \eta_0) \times 100 \quad (3)$$

As shown in Fig. S5d,† at a weight percentage of 1%, for the lubricants formulated with all the branched polymer samples

of EHMA, the SSI values are only up to 0.6, even being negative for PEHMA₅₀-DVB_{0.75}. More extraordinarily, all the formulated lubricants exhibit a shear thickening ability. In particular, the shear thickening of PEHMA₅₀-DVB_{0.75} is up to 12.7%. This is very beneficial for applications under high shear stress conditions and can compensate for the thinning of the lubricant by shear. In contrast, for linearly structured PEHMA₆₀₀, a significant KV loss of 11.2% after 30 KO cycles can be observed, with an increased SSI value of 1.2. This shows that the sample is not suitable for high-grade lubricants, and needs additives with high shear stability. Furthermore, the commercial VII TK-chem V6545 shows even worse shear stability, with a severe KV loss of 24.5% after 30 KO cycles and a high SSI value of 7.0. These results demonstrate that the shear stability of polymethacrylates can be significantly enhanced when the chain topology is tuned from a linear to a branched structure.

Discussion

Brancher effect on the structure

The results of EHMA copolymerizations demonstrate that the order of branching degree from high to low with the brancher is DVB > EGDMA > VBMA. In addition, only the brancher DVB provides branched polymers with negligible linear components, further indicating that DVB is the most effective bran-

cher. Besides, the remaining pendant double bonds of VBMA units in the copolymer PEHMA₅₀-VBMA_{1.0} are all on the methacrylate side. These results suggest the preference of the styrene moiety for inserting into the polymethacrylate chain compared with the methacrylate moiety. In order to explain the experimental results more convincingly, we measured the reactivity ratios of MMA and styrene (St) under similar conditions to those of the polymerization reaction $[\text{CuBr}_2]_0/[\text{Cu}]_0/[\text{SaBOX}]_0/[\text{MMA} + \text{styrene}]_0/[\text{BPN}]_0 = 1/4/2/100/2$.

The monomer feed ratio and the copolymer composition determined from ¹H NMR are tabulated in Table 2. It can be seen that the copolymer had a higher styrene content than the feed. The parameters for determining the reactivity ratio *via* the Fineman–Ross, Mayo–Lewis and Kelen–Tudos methods were calculated from the composition data and the values are also tabulated in Table 2. The corresponding plots are shown in Fig. 7. The average reactivity ratios of the two monomers are calculated as $r_1(\text{MMA}) = 0.352$ and $r_2(\text{St}) = 1.565$, respectively, with $r_1(\text{MMA})r_2(\text{St}) = 0.551$.^{69,70} This indicates that the copolymerization of MMA with styrene is non-ideal random copolymerization, and the copolymerization tendency is greater than the self-polymerization tendency for MMA, which well explains the aforementioned results and coincides with the preference of the styrene moiety for inserting into the polymethacrylate chain compared with the methacrylate moiety. It should be noted that the loading ratio of the main monomer to brancher

Table 2 The experimental protocols^a and calculations for the reactivity ratio of MMA and styrene *via* Fineman–Ross, Mayo–Lewis and Kelen–Tudos methods

MMA : styrene		Fineman–Ross		Kelen–Tudos ^b		Mayo–Lewis	
Monomer feed	Copolymer composition	<i>G</i>	<i>X</i>	ζ	η	<i>f</i>	1/ <i>F</i>
40 : 60	18.92 : 81.08	-1.2981	0.6688	0.1821	-0.3534	0.3950	4.2857
50 : 50	34.07 : 65.93	-0.9338	1.9288	0.3910	-0.1893	0.9983	1.9355
80 : 20	52.76 : 47.24	0.2503	5.1374	0.6310	0.0307	2.3952	1.1167
70 : 30	70.00 : 30.00	3.2063	13.4935	0.8179	0.1944	5.6111	0.4286
—	—	$r_1(\text{MMA}) = 0.354$	—	$r_1(\text{MMA}) = 0.350$	—	$r_1(\text{MMA}) = 0.353$	—
—	—	$r_2(\text{St}) = 1.572$	—	$r_2(\text{St}) = 1.556$	—	$r_2(\text{St}) = 1.566$	—

Average values: $r_1(\text{MMA}) = 0.352 \pm 0.002$; $r_2(\text{St}) = 1.565 \pm 0.007$

^a Copolymerization conditions: $[\text{CuBr}_2]_0/[\text{Cu}]_0/[\text{SaBOX}]_0/[\text{MMA} + \text{styrene}]_0/[\text{BPN}]_0 = 1/4/2/100/2$, THF/DMSO (v/v = 7/1) as the solvent, $[\text{MMA} + \text{styrene}]_0 = 1.7 \text{ M}$, $n(\text{MMA} + \text{styrene}) = 4 \text{ mmol}$, $V_{\text{total}} = 2.4 \text{ mL}$, 30 °C, and conv. (MMA or styrene) < 20%. ^b $\alpha = 3.004$.

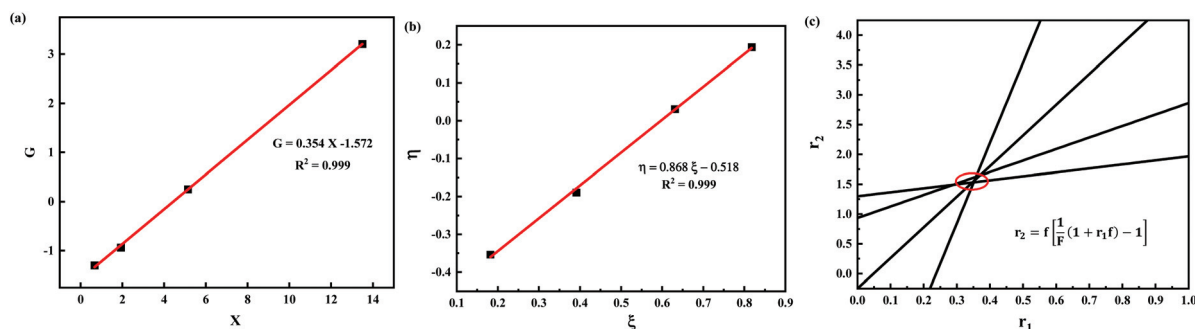


Fig. 7 Plots for calculating the reactivity ratio of MMA and styrene: (a) Fineman–Ross plot, (b) Kelen–Tudos plot, and (c) Mayo–Lewis plot.

is 50/1.0 or 50/0.75, and thus the polymerization process is dominated by continuous polymerization of EHMA. In a reaction system where the methacrylate radical is much more than the styrenic radical, one styrene double bond is more likely to be incorporated into the polymer chain than one double bond of methacrylate. Therefore, DVB is a more effective brancher than EGDMA, as the former is more easily incorporated into the polymer chain and the pendant styrene double bond more readily reacts with the methacrylate radical to form a branched structure. The styrene double bond in VBMA inserts into the polymer chain preferentially rather than into the one on the methacrylate side. Moreover, VBMA units are concentrated in the forepart of the polymer chain, and the pendant methacrylate group is easily wrapped by the polymer chain as it is difficult to react timely to form a branched structure, which is consistent with the high content of the remaining pendant methacrylate double bonds (44%) in the resultant PEHMA₅₀-VBMA_{1.0}. Therefore, DVB is the most efficient brancher, while VBMA is the worst one. On the other hand, the brancher DVB produces branched polymers possessing “X”-like branch-linkages, while the branchers EGDMA and VBMA provide “T”-like branch-linkages. This result is also consistent with the reactivity ratios of MMA and St mentioned above, which indicates that it is more facile to incorporate one pendant styrene double bond (earlier) into another polymethacrylate chain than one pendant double bond of methacrylate to form a branched structure. It is noted that the values of the reactivity ratios we obtained are somewhat different from those in literature reports,^{71–74} possibly because the polymerization temperature in this work (30 °C) is lower than those commonly employed in literature reports and the catalytic system we employed is different from those widely used.

Brancher effect on the performance as a VII

It is worth noting that among all the branched polymers, PEHMA₅₀-DVB_{0.75} exhibits the most outstanding performance, with the best viscosity thickening power, the highest viscosity index, the most excellent shear stability and even shear thickening ability. This probably derives from the high molecular weight and special topological structure of the DVB-corresponding polymer. First, the higher molecular weight of PEHMA₅₀-DVB_{0.75} than those of other branched polymers endows it with better viscosity thickening power and VI improving capacity, both of which are usually enhanced with molecular weight.⁵⁸ Furthermore, as mentioned above, the branched chain of PEHMA₅₀-DVB_{0.75} derived from an “X”-like linkage contains about 25 monomer units, which is much shorter than the branch of PEHMA₅₀-EGDMA_{1.0} or PEHMA₅₀-VBMA_{1.0} from a “T”-like linkage bearing about 48 monomer units. Compared with other branched polymers of EHMA, PEHMA₅₀-DVB_{0.75} with an “X”-like linkage has a more approximately spherical structure, resulting in fewer interactions among the branched chains (chain aggregation and entwinement). Thus, the PEHMA₅₀-DVB_{0.75} macromolecule moves and extends more freely at high temperature, which facilitates its interaction with base oil molecules and increases the internal

friction. As a result, among the branched polymers, PEHMA₅₀-DVB_{0.75} exhibits the best VI improving power and viscosity thickening ability. Its ability to improve the VI value is comparable to that of linear PEHMA₆₀₀ with higher molecular weight. This is consistent with the $[\eta]$ plots (Fig. 4), which show that the branched polymethacrylates produced using DVB as the brancher have higher viscosity than those obtained employing EGDMA and VBMA at the same molecular weight. On the other hand, under shear conditions, all the polymer chains stretch.⁷⁵ In this case, compared with linear and branched polymers containing “T”-like branch-linkages, the topology of PEHMA₅₀-DVB_{0.75} with an “X”-like linkage and shorter branches is more compact (Fig. 1), which provides excellent shear stability owing to the insensitivity of their molecular weight toward chain breakage. Shear thinning is common for lubricants with polymer VIIs. However, it has been reported that the lubricant with a branched polymer as the VII exhibits a unique performance of shear thickening.^{57,58} We speculate that the shear thickening performance of PEHMA₅₀-DVB_{0.75} is caused by two aspects in addition to the variations in the measurements. First, PEHMA₅₀-DVB_{0.75} has a branched structure with an “X”-like branch-linkage, resulting in very high shear stability and no significant chain breakage during measurements. Besides, after 30 KO cycles under the mechanical shear conditions, the branched polymer is more stretched, which is conducive to the penetration or winding of its branched and main chains with the base oil molecules.⁶⁹ This leads to slightly increased internal friction and higher viscosity. Overall, PEHMA₅₀-DVB_{0.75} exhibits the best comprehensive performance in terms of VI improving capacity and shear stability among all the samples, and is potentially suitable for premium lubricants involving high shear stress conditions.

Conclusions

A series of highly oil-soluble and branched polymethacrylates have been designed and prepared *via* ATRcP of EHMA and the divinyl brancher with high efficiency, employing the bisoxazoline/copper catalyst developed by our group and focusing on the brancher effect on the structure and performance of the polymer. The order of branching degree from high to low with the brancher is DVB > EGDMA > VBMA. Besides, the brancher DVB produces branched polymers possessing “X”-like branch-linkages with negligible linear components, while the other two branchers provide polymers with “T”-like branch-linkages and considerable linear or near-linear structures. These results could be well explained by the reactivity ratios of the different double bonds in the polymerization system. PEHMA₅₀-DVB_{0.75} with “X”-like branch-linkages exhibits superiority in performance as a potential VII over those with “T”-like branch-linkages and a commercial analogue, achieving better VI improving power and viscosity thickening ability. More notably, compared with linear and other branched polymers, PEHMA₅₀-DVB_{0.75} has better shear stability, exhibiting a shear thickening ability and a negative shear stability index, which make it ideal for

potential applications as an additive of premium lubricants involving high shear stress. This work paves a new way for conveniently regulating the topology and application performance of polymethacrylate materials. The optimization of the polymerization formula and process as well as large-scale production are being promoted.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors are grateful for financial support from Youth Innovation Promotion Association CAS (No. 2020259), the National Natural Science Foundation of China (21901253 and U19B6001), and Shanghai Rising-Star Program (21QA1411200).

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