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## 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 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-linkage exhibit superiority in comprehensive performance as viscosity index improver (VII) of lubricant than 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 additive of premium lubricant involving high shear stress.

### Introduction

Highly branched polymers have become a very promising type of polymers because of their divergent three-dimensional globular structure and the large number of terminal functionalities.<sup>1-4</sup> They are suitable candidates for a variety of applications, from biomaterials and drug delivery systems<sup>5</sup> to more applied fields such as wastewater treatment,<sup>6</sup> coatings,<sup>7</sup> inkjet printing,<sup>8</sup> encapsulation technologies,<sup>9</sup> and lubricant additives (such as viscosity index improver (VII)).<sup>10</sup> The synthesis of branched polymers can be achieved by the classical polycondensation of AB<sub>n</sub>-type monomers,<sup>11-12</sup> the self-condensing vinyl polymerization of iminers,<sup>13-14</sup> the controlled radical homopolymerization of divinyl monomers,<sup>2,15</sup> or the copolymerization of a vinyl monomer with a small amount of divinyl or multivinyl brancher (Strathclyde route).<sup>16-19</sup> 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 out good promise in terms of large-scale production.

Conventional free radical polymerization (FRP) can be used for the synthesis of highly branched polymers via 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.<sup>20</sup> Numerous efforts have been devoted to preventing gelation, such as using a large amount of chain transfer agent<sup>18, 21-26</sup> or employing controlled radical polymerizations.<sup>27-30</sup> Among these strategies, atom transfer radical copolymerization (ATRCp) has received extensive attention, as its pseudo-living character offers a 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 crosslinker or brancher reported by Matyjaszewski and Armes, respectively, the experimental result combined with theoretical simulation proved that ATRP technology resulted in very low levels of intramolecular cyclization and a more homogeneous

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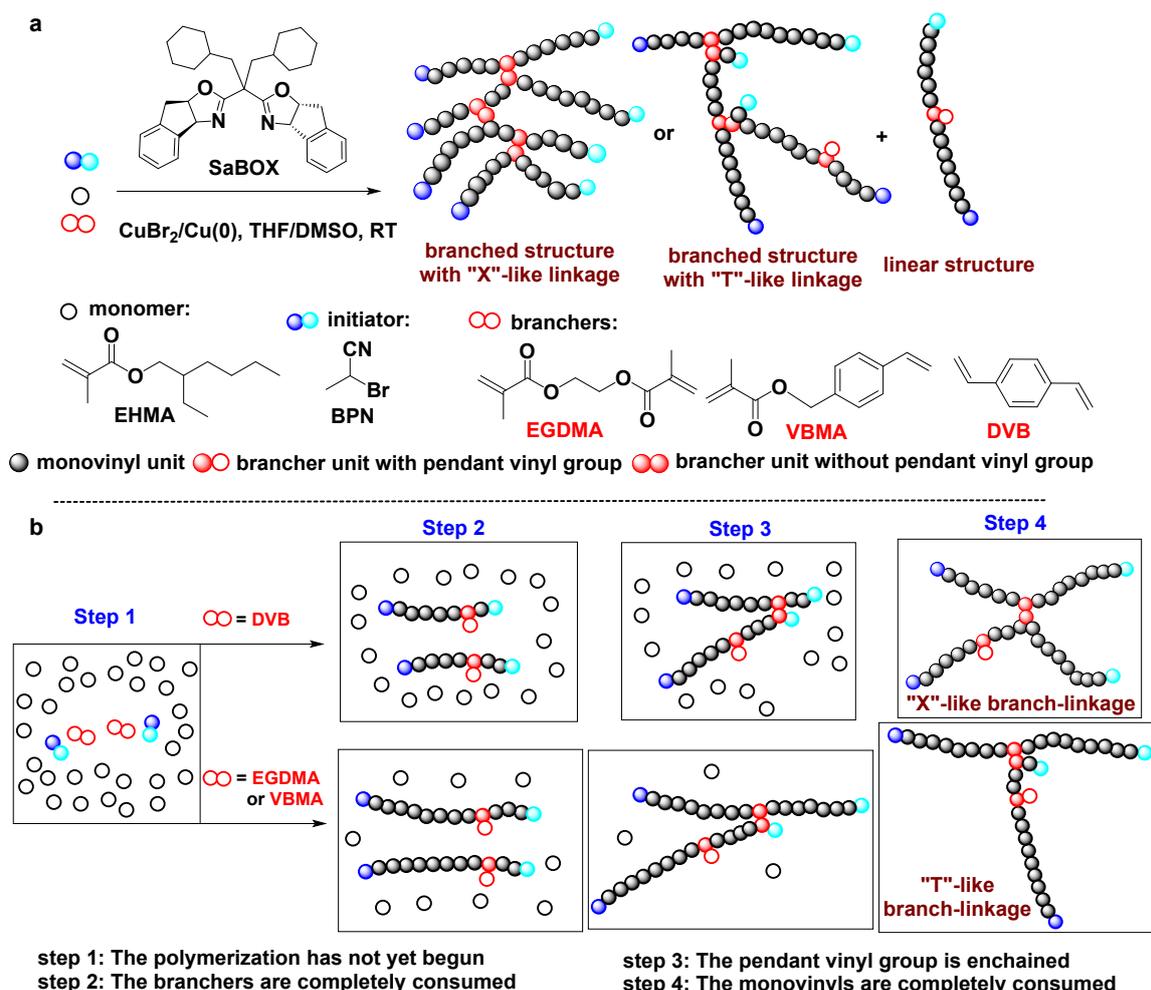
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crosslinked or branched structures compared with FRP process.<sup>31-32</sup>

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

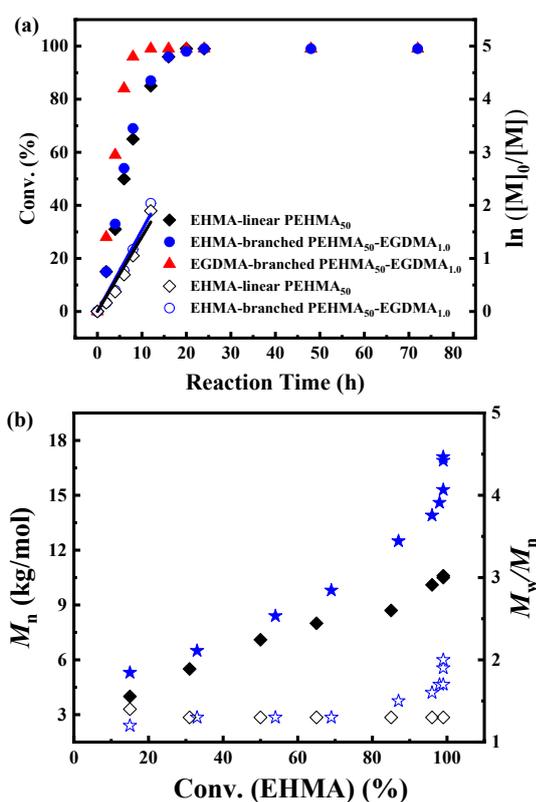
Several research groups systematically studied the synthesis of branched polymers and/or gels via the ATRCP of monovinyl monomer and divinyl brancher.<sup>31-35</sup> However, to date, most of these studies are based on the copolymerization of (methyl) methacrylate<sup>30</sup>, styrene<sup>36-37</sup> or 2-hydroxypropyl methacrylate.<sup>38-39</sup> Besides, highly branched polymers obtained by this route generally inevitably contain considerable linear components.<sup>14,30</sup> Furthermore, the effects of divinyl brancher or crosslinker 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.<sup>34-35</sup> Sherrington investigated the differing behaviors of the divinyl branchers using conventional free radical copolymerization of MMA in the presence of chain transfer agent, showing that divinyl benzene mixture produced the more regularly branched material with the narrower molar mass distribution than ethylene glycol dimethacrylate (EGDMA) and ethylene glycol diacrylate.<sup>18</sup> A very nice work reported by Jiang et al.<sup>36</sup> demonstrates the significant brancher effect on polymer branching structure in

the ATRCP of styrene with different branching agents, which mainly roots in the different polar interaction between styrene and 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. For all we know, to date, there has been no report specially on the synthesis of highly oil-soluble and branched polymethacrylates via the ATRCP of monovinyl monomer and divinyl brancher. 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 for the synthesis of highly oil-soluble and branched polymethacrylates with negligible linear components. Furthermore, it is definitely important to establish correlations between brancher reactivity and polymer structure, and between polymer structure and properties.

In this work, we focus on the effect of divinyl brancher employed in ATRcP reaction on the topology and the application performance as 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 (Figure 1a).<sup>40-45</sup> More remarkably, for the first time, it is found that brancher significantly affects not only the branching degree, but also the branch structure (Figure 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 easily-available divinyl brancher, it is very convenient to prepare various branched polymethacrylates, which prove potential VII with unique and excellent performance.

## Results

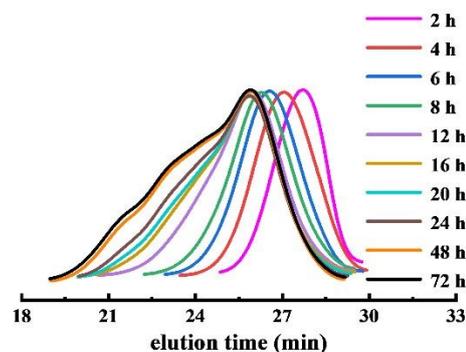
### Synthesis and structure identification of highly branched polymethacrylates



**Figure 2** ATRP kinetic data for the synthesis of PEHMA<sub>50</sub> and PEHMA<sub>50</sub>-EGDMA<sub>1.0</sub>. (a) Conversion (filled points) and  $\ln([M]_0/[M])$  (unfilled points) versus time for EHMA (blue) and EGDMA (red) during the synthesis of branched copolymer PEHMA<sub>50</sub>-EGDMA<sub>1.0</sub> as well as for EHMA during the synthesis of linear PEHMA<sub>50</sub> (black). (b)  $M_n$  (filled points) and  $M_w/M_n$  (unfilled points) versus conversion during the synthesis of PEHMA<sub>50</sub>-EGDMA<sub>1.0</sub> (blue) and PEHMA<sub>50</sub> (black).

Firstly, we conducted the supplemental activation and reducing agent (SARA) ATRcP of EHMA with EGDMA at ambient temperature employing our bisoxazoline/copper catalyst at

[EHMA]<sub>0</sub>/[EGDMA]<sub>0</sub>/[initiator]<sub>0</sub> = 50/1/1, in which 2-bromopropionitrile (BPN) and THF/DMSO are used as the initiator and the 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.<sup>30-35, 38-39</sup> 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 divinyl brancher to initiator is used. Figure 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 divinyl brancher.<sup>19, 38</sup> The conversion of EGDMA is always higher than that of EHMA might due to the presence of two reactive vinyl bonds in EGDMA. As shown in Figure 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 value ( $M_w/M_n$ ) occur 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.<sup>19,37</sup> Figure 3 shows the evolution of the differential molecular weight distribution of PEHMA<sub>50</sub>-EGDMA<sub>1.0</sub> with reaction time obtained by 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 polymers with high molecular weight and broad MW distribution.<sup>18,46</sup>



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

The branching coefficient is calculated as 0.50, according to Equation 1, where  $M_{n,b}$  and  $M_{n,l}$  are respectively the molecular weights of the branched polymer and of the linear polymer produced under the same conditions in the absence of brancher.<sup>36</sup> It is believed that the RI system underestimates the true molecular weights significantly as a result of the 3-dimensional shape of the polymers synthesized.<sup>19, 37, 47</sup> As shown in Table 1, the measured multiangle light scattering (LS) molecular weight ( $M_{n,LS} = 30.2$  kg/mol,  $M_{w,LS} = 104.1$  kg/mol) is much higher than the RI result ( $M_{n,RI} = 21.4$  kg/mol,  $M_{w,RI} = 64.2$  kg/mol), strongly supporting

formation of a highly branched architecture.<sup>48</sup> The intrinsic viscosity ( $[\eta]$ ) plot of PEHMA<sub>50</sub>-EGDMA<sub>1.0</sub> in Figure 4 is below that of linear PEHMA<sub>600</sub>. The Mark-Houwink parameter ( $\alpha$ ) for PEHMA<sub>50</sub>-EGDMA<sub>1.0</sub> is 0.35 (Table S1), which is substantially lower than that of linear polymer (0.61). These results also confirm the highly branched structure of the resultant PEHMA<sub>50</sub>-EGDMA<sub>1.0</sub>.<sup>49</sup> As shown in the <sup>1</sup>H NMR spectrum of the isolated PEHMA<sub>50</sub>-EGDMA<sub>1.0</sub>, the signals at 6.16 and 5.44 ppm are attributed to the pendant methacrylic protons in the EGDMA units (Figure S1). A comparison of the corresponding signal integrals of the copolymerization mixture reveals that 18% of EGDMA units contain pendant vinyl groups (for detailed analysis and calculation methods, see Support Information).

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

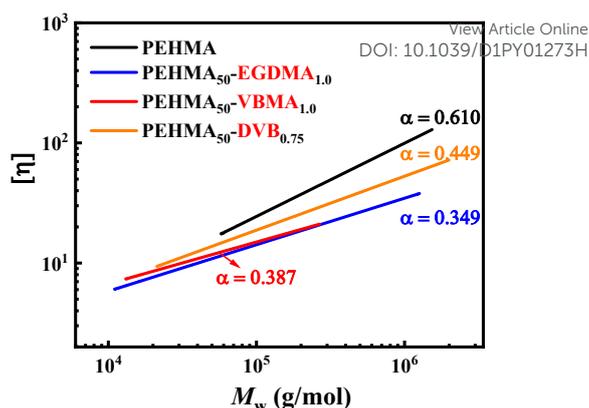


Figure 4. Intrinsic viscosity ( $[\eta]$ ) for PEHMA<sub>600</sub>, PEHMA<sub>50</sub>-EGDMA<sub>1.0</sub>, PEHMA<sub>50</sub>-DVB<sub>0.75</sub>, and PEHMA<sub>50</sub>-VBMA<sub>1.0</sub>.

Table 1. Summary of linear and branched polymers prepared with varying branchers<sup>a</sup>

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

<sup>a</sup>Reaction condition:  $[CuBr_2]/[Cu]/[SaBOX]/[EHMA]/[divinyl\ brancher]/[BPN] = 1/4/2/100/x/2$  ( $x = 2$  for EGDMA and VBMA, 1.5 for DVB), THF/DMSO ( $v/v = 7/1$ ) is used as the solvent,  $[EHMA]_0 = 1.7$  M,  $V_{total} = 28.2$  mL, 30 °C, 72 h, conv.(EHMA) > 99%. Tracing is carried out. <sup>b</sup>The ratio of residual double bonds in the brancher units, measured by <sup>1</sup>H NMR (for detailed analysis and calculation methods, see Support Information). <sup>c</sup>The closer it is to 1, the higher the branching degree, calculated based on Equation 1. <sup>d</sup>Mark-Houwink parameter determined by viscosity detector.

### Brancher effect

Subsequently, the brancher effect on polymerization process and copolymer structure is detailedly studied 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 PEHMA<sub>50</sub>-DVB<sub>1.0</sub> could not be prepared as a soluble and branched, rather than a gelled product. This result might mainly be due to that, the styrene moiety of the DVB unit is much easier to be incorporated in the EHMA polymer chain than the methacrylate moiety of EGDMA units. Besides, on steric grounds, the DVB unit might have a less propensity towards cyclization than the EGDMA unit.<sup>36, 38</sup> 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 provided completely soluble copolymer (PEHMA<sub>50</sub>-DVB<sub>0.75</sub>). Notably, the <sup>1</sup>H NMR spectrum of PEHMA<sub>50</sub>-DVB<sub>0.75</sub> indicates the complete absence of any signals due to pendant unreacted vinyl groups (Figure 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 shows that the

remaining pendant double bonds of VBMA units in the copolymer PEHMA<sub>50</sub>-VBMA<sub>1.0</sub> are all on the methacrylate side with a high content of 44% (for detailed analysis and calculation methods, see Support Information), suggesting a low branching degree (Figure S3). This result further demonstrates the preference of styrene moiety for inserting into the EHMA polymer chain compared with methacrylate moiety.

The  $M_{n,RI}$  data for the copolymers PEHMA<sub>50</sub>-DVB<sub>1.0</sub>, PEHMA<sub>50</sub>-EGDMA<sub>1.0</sub> and PEHMA<sub>50</sub>-VBMA<sub>1.0</sub> are, respectively, 34.9, 21.4, and 15.1 kg/mol; while the  $M_{n,LS}$  data are 55.2, 30.2, and 25.8 kg/mol. (Table 1). The branching coefficient for these three polymers are 0.70, 0.50 and 0.30, respectively. It is clear that the copolymer PEHMA<sub>50</sub>-DVB<sub>0.75</sub> 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 are PEHMA<sub>50</sub>-DVB<sub>0.75</sub> > PEHMA<sub>50</sub>-EGDMA<sub>1.0</sub> > PEHMA<sub>50</sub>-VBMA<sub>1.0</sub>.

As mentioned above (Figure 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 be combined with others via inter-macromolecule radical addition, the branched polymer will contain a significant amount of linear structure and its GPC elution curve should overlap with that of the linear PEHMA<sub>50</sub> obtained under the similar

conditions.<sup>19, 35, 37</sup> Remarkably, as shown in Figure 5, when VBMA is used as the brancher, the RI curve of the resultant PEHMA<sub>50</sub>-VBMA<sub>1.0</sub> mostly overlap with that of linear PEHMA<sub>50</sub> obtained in the absence of brancher, indicating that PEHMA<sub>50</sub>-VBMA<sub>1.0</sub> is dominated by linear or near-linear structure. Similarly, when EGDMA is used as the brancher, a significant portion of the RI curve of the branched products overlap with those of linear polymers, suggesting that the products contain considerable linear or near-linear components. By contrast, when the brancher DVB is employed, the GPC-RI curve of the obtained polymer has little overlap with those of the linear polymers. The multipeak splitting using Gaussian function could not distinguish the linear components,<sup>19</sup> indicating that the linear structure is negligible. These results further demonstrate that DVB is the most effective brancher.

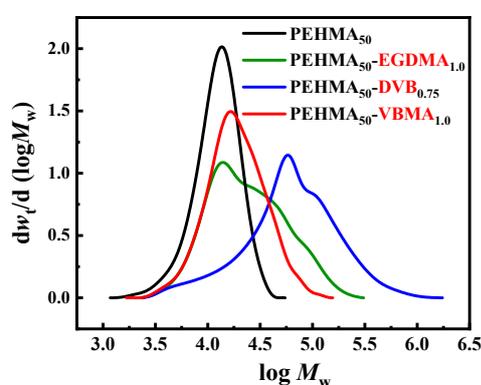


Figure 5. RI curves: PEHMA<sub>50</sub>, PEHMA<sub>50</sub>-VBMA<sub>1.0</sub>, PEHMA<sub>50</sub>-DVB<sub>0.75</sub> and PEHMA<sub>50</sub>-EGDMA<sub>1.0</sub>.

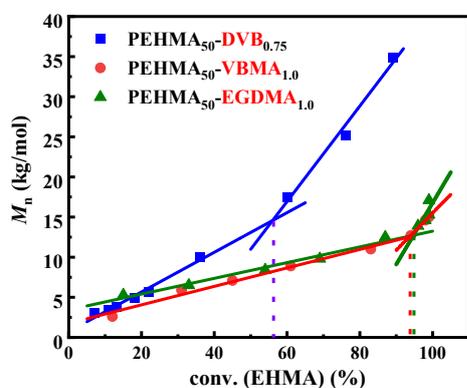


Figure 6. The curves showing  $M_n$  versus conversion obtained by RI detector for the synthesis of PEHMA<sub>50</sub>-DVB<sub>0.75</sub>, PEHMA<sub>50</sub>-EGDMA<sub>1.0</sub> and PEHMA<sub>50</sub>-VBMA<sub>1.0</sub>.

More importantly, it is deduced that the brancher not only leads to great differences in molecular weight, branching degree and components of the polymer, but also seriously affects the branch structure of the polymer. As shown in Figure 6, when EGDMA, VBMA and DVB are employed as the branchers, the steep increase of MW occurs at EHMA conversions of 96%, 94% and 56%, respectively, and meanwhile, the MW distributions rapidly widen (Figure 2b and Figure S4). The sharp rise in molecular weight and

dispersity value are generally caused by large-scale inter-macromolecular addition reactions between a macromolecule radical with a pendant double bond introduced by a divinyl brancher.<sup>19, 37-38</sup> 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 ratio of two branched chains generated by a brancher is about 24/1 and 16/1 when using EGDMA and VBMA, respectively, forming a local structure with "T"-like branch-linkage (Figure 1b). By 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 "X"-like branch-linkage (Figure 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 "X"-like linkage. It should be noted that, similar to the method by Matyjaszewski<sup>50</sup>, the models of "T"-like and "X"-like branch-linkage are proposed to clearly illustrate the whole branching process, which 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 evidences such as images are difficult to provide. The intrinsic viscosity plots of these polymers also support the difference in topological structure. As shown in Figure 4, the polymers with EGDMA and VBMA as branchers have very similar  $\alpha$  and  $[\eta]$  at the same molecular weight, while the polymer with DVB as branching agent have a relatively high  $\alpha$  value and viscosity.  $\alpha$  and  $[\eta]$  values are influenced by many factors, such as the functionality and concentration of the multifunctional monomer, the structure and the degree of the branching, as well as the concentration of the polymer solution.<sup>17, 51</sup> Both  $\alpha$  and  $[\eta]$  values are generally negatively correlated with the branching degree and/or the length of branched chain.<sup>4, 52-54</sup> The higher  $\alpha$  and  $[\eta]$  of PEHMA<sub>50</sub>-DVB<sub>0.75</sub> indicate that longer branched chains contribute more to the reduction of polymer viscosity and  $\alpha$  value than more branched chains for this branched polymer series. These differences in topology and viscosity prefigure that the branched polymers obtained using different branchers will exhibit varying performances as VII of lubricant.

#### The Performance as viscosity index improver

Viscosity index improver is indispensable for the formulation and performance design of multigrade engine oils, hydraulic fluids, and transmission fluids. Fuel efficiency of the engine is highly dependent on the ability of polymer with 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.<sup>55</sup> 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 breakages under the high mechanical shear conditions (poor shear stability).<sup>56-59</sup> 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 composition.<sup>60-61</sup>

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 Figure S5). The absolute weight-average molecular weight of linear PEHMA<sub>50</sub> ( $M_{w,LS} = 18.1$  kg/mol) is far lower than those of branched polymers, so it is unfair to compare its performance as VII with that of branched polymers. Therefore, the linear polymer PEHMA<sub>600</sub> (Table 1), with a molecular weight ( $M_{w,LS} = 234.5$  kg/mol) comparable to those of branched polymers, was synthesized and also applied as potential VIIs. 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 polymethacrylate were blended into the base oil 150N<sup>56, 62-64</sup> (for more information of base oil 150N, see Support Information) 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 PEHMA<sub>50</sub>-DVB<sub>0.75</sub> and PEHMA<sub>50</sub>-VBMA<sub>1.0</sub> have a clear appearance. As shown in Figure S5a, the addition of 5 wt% of linear PEHMA<sub>600</sub> obtains formulated lubricant with a hazy appearance (IV), while the addition of 5 wt% of branched PEHMA<sub>50</sub>-DVB<sub>0.75</sub> still affords highly transparent formulated lubricant (II), which is consistent with the results of transmittance test (Table S1). These results demonstrate the solubility advantage of branched polymers over linear polymers with similar molecular weights. The solubility of VII influences not only the appearance but also the performance stability of lubricant.<sup>65-68</sup> Besides the polymers, no other additives were applied in the lubricant formulations.

$\Delta VI$  and  $\Delta KV100$  refer to the variations in viscosity index (VI) and kinematic viscosity of lubricant at 100 °C (KV100) after adding polymer VII, respectively, which are commonly used to assess the VI improving power and viscosity thickening capacity of polymer VII. As shown in Figures S5b and S5c, compared with the branched polymers obtained using other branchers, PEHMA<sub>50</sub>-DVB<sub>0.75</sub> exhibits better viscosity thickening ability and VI improving capacity, with higher  $\Delta VI$  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.<sup>56, 58-59</sup> The linear PEHMA<sub>600</sub> excels in viscosity thickening capacity. However, despite its high molecular weight, PEHMA<sub>600</sub> does not show obvious superiority in improving VI value (Figure S5b), compared with branched PEHMA<sub>50</sub>-DVB<sub>0.75</sub>, especially at 1 wt% concentration ( $\Delta VI = 22$  versus 21). Although the VI value obtained by PEHMA<sub>600</sub> is higher than that of branched PEHMA<sub>50</sub>-DVB<sub>0.75</sub> 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 literatures.<sup>56, 58</sup> Notably, the commercial TK-chem V6545 performs inferiorly, with respect to viscosity thickening ability and VI improving power, compared to the branched PEHMA<sub>50</sub>-DVB<sub>0.75</sub>.

To examine the effect of the chain topology on the shear stability of the polymers, the Kurt Orbahn (KO) test (for details, see Support Information), which is commonly used for the shear stability testing of VIIs, was conducted on these lubricant samples.<sup>56-59</sup> Two commonly used parameters, the percentage kinematic viscosity loss (KV100 loss (%), Equation 2) and shear stability index (SSI, Equation 3), are used to quantify the macromolecular shear degradation. The smaller they are, the higher the shear stability is.  $\eta_f$  is the kinematic viscosity of the fresh unsheared lubricant,  $\eta_s$  is the kinematic viscosity of the sheared lubricant and  $\eta_0$  is the kinematic viscosity of the base oil at 100 °C.

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

$$SSI = (\eta_f - \eta_s) / (\eta_f - \eta_0) \times 100 \quad \text{(Equation 3)}$$

As shown in Figure 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 PEHMA<sub>50</sub>-DVB<sub>0.75</sub>. More extraordinarily, all the formulated lubricants exhibit shear thickening ability. Especially, the shear thickening of PEHMA<sub>50</sub>-DVB<sub>0.75</sub> 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. By contrast, for linearly structured PEHMA<sub>600</sub>, significant KV loss of 11.2% after 30 KO cycles can be observed, with an increased SSI value of 1.2. It shows that the sample is not suitable for high-grade lubricant, which needs additives with high shear stability. Furthermore, the commercial VII TK-chem V6545 shows even worse shear stability, with 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

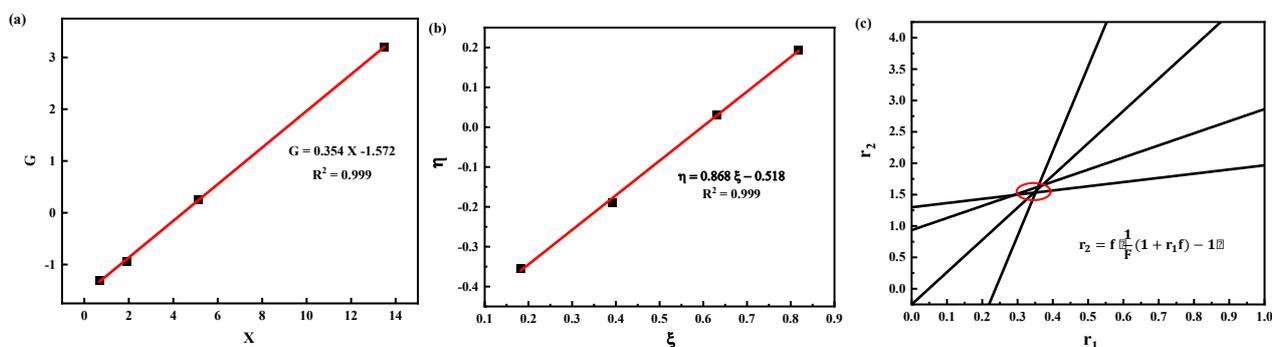
branched polymers with negligible linear components, further indicating that DVB is the most effective brancher. Besides, the remaining pendant double bonds of VBMA units in the copolymer PEHMA<sub>50</sub>-VBMA<sub>1.0</sub> are all on the methacrylate side. These results suggest the preference of styrene moiety for inserting into the

polymethacrylate chain compared with methacrylate moiety. In order to explain the experimental results more convincingly, we measured the reactivity ratios of MMA and styrene (St) under the similar conditions as the polymerization reaction ([CuBr<sub>2</sub>]<sub>0</sub>/[Cu]<sub>0</sub>/[SaBOX]<sub>0</sub>/[MMA + styrene]<sub>0</sub>/[BPN]<sub>0</sub> = 1/4/2/100/2).

**Table 2.** The experimental protocols<sup>a</sup> 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 <sup>b</sup>		Mayo-Lewis	
Monomer Feed	Copolymer Composition	G	X	ζ	η	f	1/F
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 <sub>1</sub> (MMA) = 0.354 r <sub>2</sub> (St) = 1.572		r <sub>1</sub> (MMA) = 0.350 r <sub>2</sub> (St) = 1.556		r <sub>1</sub> (MMA) = 0.353 r <sub>2</sub> (St) = 1.566	
Average values: r <sub>1</sub> (MMA) = 0.352 ± 0.002; r <sub>2</sub> (St) = 1.565 ± 0.007							

<sup>a</sup>Copolymerization condition: [CuBr<sub>2</sub>]<sub>0</sub>/[Cu]<sub>0</sub>/[SaBOX]<sub>0</sub>/[MMA + styrene]<sub>0</sub>/[BPN]<sub>0</sub> = 1/4/2/100/2, THF/DMSO (v/v = 7/1) is used as the solvent, [MMA + styrene]<sub>0</sub> = 1.7 M, n(MMA + styrene) = 4 mmol, V<sub>total</sub> = 2.4 mL, 30 °C, conv.(MMA or styrene) < 20%. <sup>b</sup>α = 3.004.



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

The monomer feed ratio and the copolymer composition determined from <sup>1</sup>H NMR are tabulated in Table 2. It can be seen that the copolymer had higher styrene content than the feed. The parameters for determining the reactivity ratio via 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 as Figure 7. The average reactivity ratios of the two monomers are calculated as r<sub>1</sub>(MMA) = 0.352 and r<sub>2</sub>(St) = 1.565, respectively, with r<sub>1</sub>(MMA)r<sub>2</sub>(St) = 0.551.<sup>69-70</sup> 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 coincide with the preference of styrene moiety for inserting into the polymethacrylate chain compared with methacrylate moiety. It should be noted that the loading ratio of main monomer to brancher 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 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 branched structure. The styrene double bond in VBMA inserts into the polymer chain preferentially to the one on the methacrylate side. Moreover, VBMA units are concentrated in the forefront of the polymer chain, and the pendant methacrylate group is easily wrapped by the polymer chain as it is difficult to react to form branched structure timely, which is consistent with the high content of remaining pendant methacrylate double bonds (44%) in the resultant PEHMA<sub>50</sub>-VBMA<sub>1.0</sub>. 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-linkage, while the branchers EGDMA and VBMA provide "T"-like branch-linkage. This result is also consistent with the reactivity ratios of MMA and St mentioned above, which indicates that one pendant styrene double bond is more facile (earlier) to incorporate into another polymethacrylate chain than one pendant double bond of methacrylate to form branched structure. It is noted that the values of the reactivity ratios we obtained are somewhat different from

those in literatures<sup>71-74</sup>, possibly because the polymerization temperature in this work (30 °C) is lower than that commonly employed in literatures and the catalytic system we employ is different from those widely used.

### Brancher effect on the performance as VII

It is worth noting that among all the branched polymers, PEHMA<sub>50</sub>-DVB<sub>0.75</sub> exhibits the most outstanding performance, with the best viscosity thickening power, the highest viscosity index, the most excellent shear stability and even exhibiting 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 PEHMA<sub>50</sub>-DVB<sub>0.75</sub> than those of other branched polymers, endows it better viscosity thickening power and VI improving capacity, both of which are usually enhanced with molecular weight.<sup>58</sup> Furthermore, as mentioned above, the branched chain of PEHMA<sub>50</sub>-DVB<sub>0.75</sub> derived from a "X"-like linkage contains about 25 monomer units, which is much shorter than the branch of PEHMA<sub>50</sub>-EGDMA<sub>1.0</sub> or PEHMA<sub>50</sub>-VBMA<sub>1.0</sub> from "T"-like linkage bearing about 48 monomer units. Compared with other branched polymers of EHMA, PEHMA<sub>50</sub>-DVB<sub>0.75</sub> with "X"-like linkage has a more approximately spherical structure, resulting in fewer interactions among the branched chains (chain aggregation and entwinement). And thus, the PEHMA<sub>50</sub>-DVB<sub>0.75</sub> macromolecule moves and extends more freely at high temperature, which facilitates its interaction with base oil molecules and increase the internal friction. As a result, among the branched polymers, PEHMA<sub>50</sub>-DVB<sub>0.75</sub> exhibits the best VI improving power and viscosity thickening ability. And even, its ability to improve VI value is comparable to that of linear PEHMA<sub>600</sub> with higher molecular weight. This is consistent with the  $[\eta]$  plots (Figure 4), which show that the branched polymethacrylates produced using DVB as 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.<sup>75</sup> In this case, compared with linear and branched polymers containing "T"-like branch-linkage, the topology of PEHMA<sub>50</sub>-DVB<sub>0.75</sub> with "X"-like linkage and shorter branches is more compact (Figure 1), which provides the excellent shear stability owing to the insensitivity of their molecular weight toward chain breakage. Shear thinning is common for lubricants with polymer VII. However, it has been reported that the lubricant with branched polymer as VII exhibits a unique performance of shear thickening.<sup>57-58</sup> We speculate that the shear thickening performance of PEHMA<sub>50</sub>-DVB<sub>0.75</sub> are caused by two aspects in addition to the variations in the measurement. First, PEHMA<sub>50</sub>-DVB<sub>0.75</sub> has branched structure with "X"-like branch-linkage, resulting in very high shear stability and no significant chain breakage during measurement. 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.<sup>69</sup> This leads to slightly increased internal friction and higher viscosity. Taken overall, PEHMA<sub>50</sub>-DVB<sub>0.75</sub> exhibits the best comprehensive

performance in terming of VI improving capacity and shear stability among all the samples, and is potentially suitable for premium lubricant 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 divinyl brancher with high efficiency, employing the bisoxazoline/copper catalyst developed by our group and focusing on the brancher effect on the structure-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 provides 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. PEHMA<sub>50</sub>-DVB<sub>0.75</sub> with "X"-like branch-linkages exhibits superiority in performance as potential VIIs over those with "T"-like branch-linkages and a commercial analogue, achieving the better VI improving power and viscosity thickening ability. More notably, compared with linear and other branched polymers, PEHMA<sub>50</sub>-DVB<sub>0.75</sub> has better shear stability, exhibiting a shear thickening ability and a negative shear stability index, which make it ideal for the potential applications as additive of premium lubricant involving high shear stress. This work paves a new way for conveniently regulating the topology and application performance of polymethacrylates materials. The optimization of polymerization formula and process as well as the large-scale production are being promoted.

## Conflicts of interest

There are no conflicts to declare.

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