Soft Elastomers via Introduction of Poly(butyl acrylate) "Diluent" to Poly(hydroxyethyl acrylate)-Based Gel Networks

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S *Supporting Information*

ABSTRACT: We report a new strategy for the synthesis of stable and well-defined supersoft elastomers. First, four-arm star-like polymers, poly-(trimethylsilyloxyethyl acrylate), were synthesized and cross-linked to form a relatively uniform polymer gel network. Second, short poly(n-butyl acrylate) side chains were grown from the initiating sites along the network backbone via atom transfer radical polymerization. These soft side chains act as low molecular weight "diluent" that "swells" the cross-linked polyHEA network, but cannot be leached from it. Using this strategy, materials with shear modulus less than 5 kPa were prepared and the effect of grafted side chain fraction on their mechanical properties was explored.
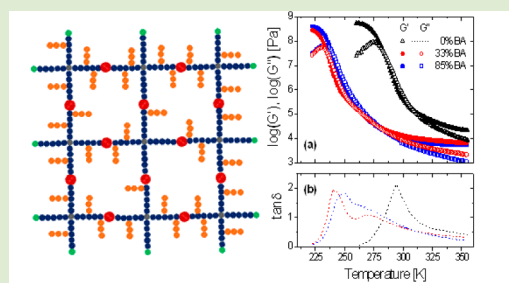
supersoft elastomers with shear modulus less than 5 kPa

The term elastomer is derived from the words elastic and polymer, and commonly used to describe a cross-linked amorphous polymer with a glass temperature well below ambient temperatures. As their name implies, these materials (also known as rubbers) are elastic, that is, they are reversibly extendable up to several times their original length and have a low Young's modulus value, typically in the order of 1 MPa. For comparison, solid materials such as steel, have a Young's modulus in the order of 100 GPa. Thus, common elastomeric materials are much softer and more deformable than typical solids. These unique features lead to a number of widespread applications for elastomers, but sometimes even softer materials are needed. Since the elastomeric properties originate in the cross-linked nature of these amorphous polymers, the elastic modulus of a given elastomer can be controlled by fine-tuning of the cross-linking density.[1] Weakly cross-linked elastomers have elasticity similar to that of the rubbery plateau of the corresponding linear polymers, while the modulus of densely cross-linked elastomers may be significantly higher. There is no simple way to prepare stable elastomers, with moduli lower than the rubbery plateau value of corresponding polymers. One possible approach is to swell a weakly cross-linked system with a good solvent for the matrix polymer, that is, to prepare a gel. Such materials can be extremely soft, with elastic modulus down to kPa.[2] Unfortunately, these solvent swollen gels are not stable, due to the potential evaporation of solvents even at ambient conditions and therefore their practical applications as elastic materials are rather limited.

As shown recently,[3] this problem may be overcome using an alternative approach. Instead of creating a network of swollen cross-linked linear polymer chains, bottlebrush macromolecules[4−6] with a very long backbone and densely grafted short poly(n-butyl acrylate) (polyBA) side chains were subsequently cross-linked. The new materials obtained in this way were called supersoft elastomers, as they showed a plateau modulus of only a few kPa,[3,7] which is orders of magnitude lower than that seen for typical polymeric rubbers, and comparable to the values characteristic for swollen hydrogels. A possible phenomenological explanation[3] for this softness is that these materials behave as swollen cross-linked networks, where the role of "diluent solvent molecules" is played by the soft polyBA side chains. These chains are short and do not entangle, but because they are covalently attached to the matrix, they provide stability against evaporation or deformation, while preventing the networks from collapsing. This combination of unique properties makes the bottlebrush-based supersoft elastomers extremely promising candidates for a number of applications.[3,8,9] However, some limitations in the above-described approach should be also considered. Most importantly, as the cross-linked network was prepared by heat treatment (annealing at 120 °C) or spontaneous cross-linking of the bottlebrush polymers during the polymerization at relatively high monomer conversion,[3,7] limited control on the cross-linking process could be achieved. This could also affect the mobility of the side chains and the linear backbone, thereby affecting the viscoelastic properties of formed network.

To overcome this problem, in this article we present a new method for the synthesis of stable and well-defined supersoft elastomers, by preparing a relatively uniformly cross-linked network first, and then growing short side chains along the network backbones. Atom transfer radical polymerization, ATRP,[10−16] allows the preparation of gel networks with more evenly distributed cross-linking points along the polymer chains than conventional radical polymerization.[17] The resulting

Scheme 1. Supersoft Elastomer via Introduction of Poly(*n*-butyl acrylate) "Diluent" to Poly(hydroxyethyl acrylate)-Based Gel Network
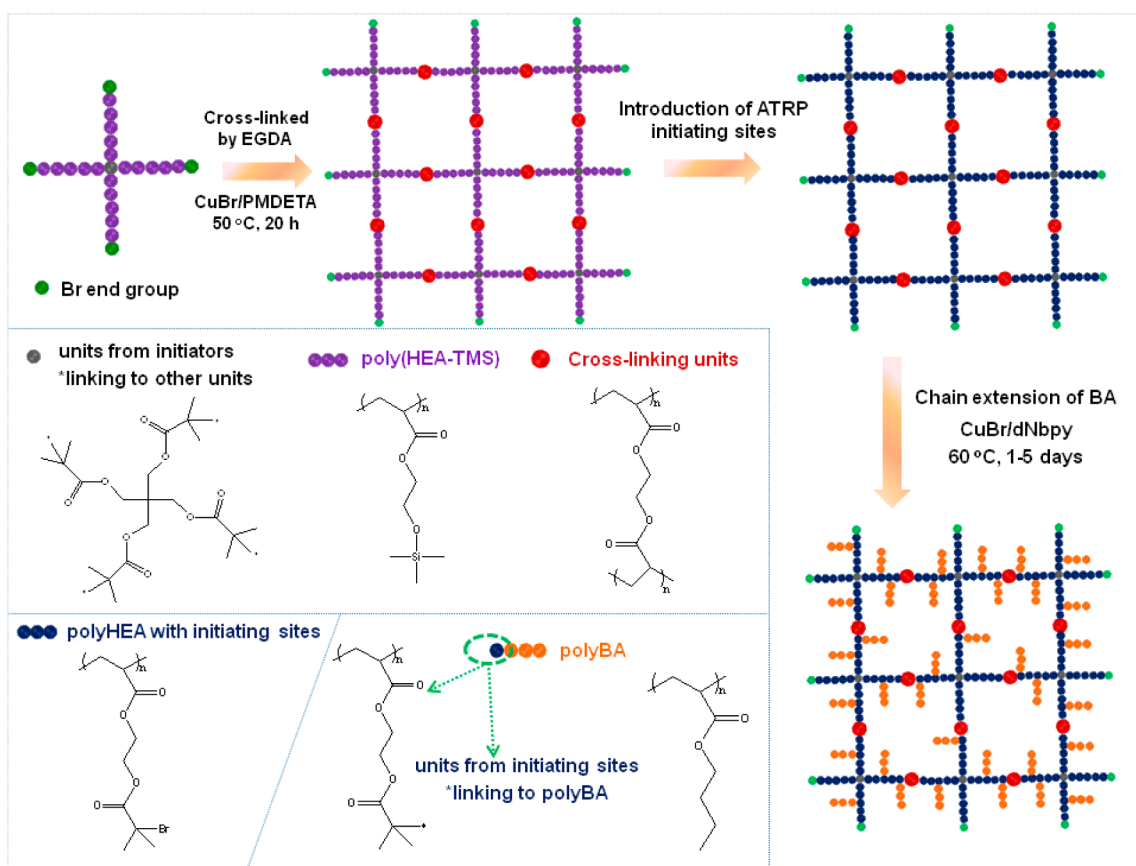
higher degree of network homogeneity would lead to a high swelling ratio for the generated network,[18−20] which is important for the successful introduction of soft side chains into the polymeric network. Thus, we used ATRP to prepare cross-linked gels, which were then used as precursors for synthesis of supersoft elastomers. Our strategy is schematically shown in Scheme 1. First, four-arm star-like polymers, poly(trimethylsilyloxyethyl acrylate) (polyHEA-TMS), were synthesized via a "core-first" method[21−24] starting from a tetrafunctional ATRP initiator. These star polymers were then cross-linked with a divinyl cross-linker, ethylene glycol diacrylate (EGDA), to form a relatively uniformly cross-linked gel network.[25,26]

In the next step, 2-bromoisobutyrate groups were introduced to the backbone of the gel network through the reaction of trimethylsilyloxy with 2-bromoisobutyryl bromide. Finally, poly(*n*-butyl acrylate) (polyBA) was grown from the initiating sites along the backbone via ATRP and short polyBA side chains were introduced in the network. Using this strategy, supersoft elastomers with shear modulus less than 5 kPa were prepared and the effect of grafted side chain fraction on their mechanical properties was explored.

PolyHEA-based gel sample H1 was used as precursor for the preparation of the supersoft elastomers. Detail compositions and synthetic procedures for this gel are summarized in the Supporting Information. 4-Arm star polymers were synthesized in a separate step and purified to remove any remaining HEA-TMS monomers before cross-linking with EGDA. The 4-arm poly(HEA-TMS) star polymers prepared by ATRP had a narrow molecular weight distribution (Figure S1, Supporting Information) and the average degree of polymerization (DP) of poly(HEA-TMS) arm was about 135. Due to the similar length of each arm, a relatively homogeneous polymer gel network was expected after the cross-linking of star polymers with EGDA. This can be supported by the relatively high swelling ratio of the formed cross-linked gels, about 14 in THF. The gel samples were then modified and ATRP initiating sites were introduced to the backbone (H1−Br) to grow polyBA side chains from the polymer network. During the chain extension of BA, 10 mol % ethyl 2-bromoisobutyrate, EBiB, was used as co-initiator to follow the independent and concurrent growth of linear polyBA chains.

By controlling the polymerization time, two elastomeric materials, H1-BA1 and H1-BA2 containing, respectively, 33 and 85% polyBA side chains fraction (as estimated by gravimetric analysis) were prepared. A common way to estimate the length of the grafted side chains is to perform a GPC analysis of the free polyBA polymers that have formed in the sample media during the grafting process. The results of such measurements are presented in Table 1. Furthermore, solid state NMR was used to estimate the average chain length of the grafted polyBA side chains, by quantification of the signal at 25.6 ppm (red arrow in Figure S3) assigned to methyl groups at the reacted ATRP initiating site, from which polyBA was grafted, and the signal at 14.3 ppm assigned to the methyl groups of butyl group at each BA repeat unit in the grafted chains (blue arrow in Figure S3). Thus, by dividing the area of the peak at 14.3 ppm that is proportional to the total number of BA group in the system to the area of the peak at 25.6 ppm that is proportional to the number of grafted polyBA chains, we estimated the

Table 1. Characterization Data for PolyHEA-Based Gel Network Containing PolyBA Side Chains[a]
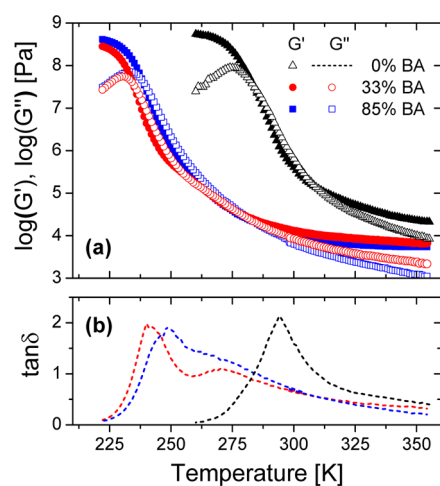
sample	starting gels	grafted polyBA fraction[b]	M_n of free polyBA[c]	M_w/M_n of free polyBA[c]	M_n of grafted polyBA[d]
H1-BA1	H1-Br	33%	2900	1.19	2200
H1-BA2	H1-Br	85%	8200	1.16	8600

[a]Polymerization conditions: $[BA]_0/[ATRP$ initiating sites from polyHEA gels, $H1\text{-}Br]_0/[EBiB]_0/[CuBr]_0/[CuBr_2]_0/[dNbpy]_0 = 406/1/0.1/0.475/0.025/1$, 60 °C; detail reaction conditions are summarized in Supporting Information. [b]Grafted polyBA fraction determined by gravimetric analysis. [c]Number-average molecular weight M_n and polydispersity index M_w/M_n of free polyBA chains determined by THF GPC with RI detector. [d]Number-average molecular weight M_n of grafted polyBA chains determined by solid state NMR.

average molecular weight of the grafted polyBA side chains. This approach has the advantage, that the T1 relaxation of methyl sites in the solid state is predominantly driven by the methyl rotation, which can be expected to be similar for the two sites. More details on the NMR studies are presented in the Supporting Information and the results of the polyBA side chain quantification are summarized in Table 1.

The molecular weights of the grafted chains measured by NMR are in agreement with that of the free polyBA chains measured by GPC. Combining the NMR results on the average length of the grafted chains and the gravimetrically determined polyBA content of the samples, the relative density of the grafting sites can be estimated to be approximately 0.06 polyBA chains/HEA monomeric unit for H1-BA1 and 0.16 polyBA chains/HEA monomeric unit for H1-BA2. The low initiation efficiency may be caused by the relatively limited accessibility and space available for polyBA chains to grow inside the gel network.

Next, the dynamic mechanical analysis (DMA) was performed to characterize the mechanical properties of the newly prepared materials. Figure 1 shows the temperature dependencies of the real (G') and imaginary (G'') parts of the

shear modulus and their ratio $\tan\delta = G''/G'$ for the samples H1-BA1 and H1-BA2 with 33% and 85% fractions of grafted polyBA. The data for the starting polyHEA based network H1−Br that does not have any grafted polyBA side chains are also shown for comparison.

All materials show a behavior rather typical for cross-linked elastomers, or rubbers, with high values of G' in the glassy state at low temperatures, followed by a glass transition manifested by a sharp decrease in G' and maximum in $\tan \delta$, and finally, a long rubbery plateau of G' at high temperatures. However, it can be seen that with increasing the polyBA fraction from 0 to 33% and to 85% the samples become softer and the value of the storage modulus G' in the rubbery plateau region at high temperatures decreases down to 3.8 kPa for the H1-BA2 that is grafted with more and longer ($M_n = 8600$) polyBA chains. This value is close to that reported earlier for supersoft elastomers based on cross-linked molecular brushes and could be attributed to the relatively large fraction of the short dangling polyBA chains in the system. Such chains provide sufficient mobility, making the material extremely soft. As discussed above, the side chains can be considered as low molecular weight diluent that "swells" the cross-linked polyHEA network. Furthermore, the starting network exhibited glass temperature, T_g, of around 290 K, but after grafting the polyBA, the glass temperature at around 235 K dominates. Nevertheless, the plot of $\tan \delta$ versus T (Figure 1b) shows also a second peak at around 270 K that could correspond to the backbone T_g. Thus, the backbone T_g in the grafted sample is significantly lower than that measured in the pristine polyHEA network. Similarly, the T_g of the polyBA side chains is higher than what is commonly observed for polyBA homopolymers, that is, ~220 K. The likely reason for this alternation is the higher restriction on the local segmental modes of the grafted PBA by the less mobile backbone. These observations are consistent with the results of a recent study, which indicated that the bottlebrush architecture imparts dynamic homogeneity to the backbone and side chain dynamics.[27]

The viscoelastic spectra that characterize the mechanical behavior of the materials in a broad frequency range were determined for both H1-BA1 and H1-BA2 and are shown in Figure 2. These master curves for G' and G'' were constructed using the time−temperature superposition (tTs) principle, that is, shifting the data recorded at various temperatures along the
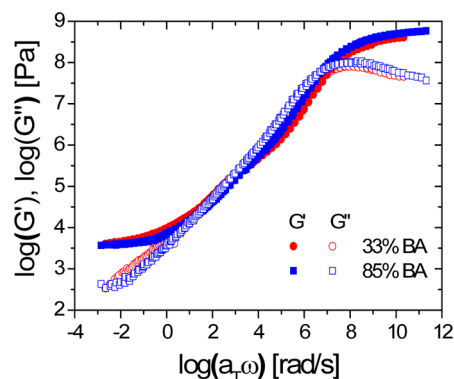

Figure 1. (a) Temperature dependence of the shear moduli G' and G'' of the starting polyHEA-based gel H1-Br (triangles) and for the samples H1-BA1 (circles) and H1-BA2 polyHEA (squares) containing, respectively, 33 and 85% of grafted polyBA fractions; (b) temperature dependence of the corresponding $\tan \delta$. The measurements were performed at constant frequency of $\omega = 10$ rad/s.

Figure 2. Plots of the logarithm of $G'(\omega)$ and $G''(\omega)$ vs the reduced frequency log $\alpha_T\omega$ for the samples H1-BA1 (circles) and H1-BA2 polyHEA (squares) containing respectively 33 and 85% of grafted polyBA fractions. The curves are constructed for reference temperature, $T_{ref} = 293$ K.

frequency coordinate. The temperature dependence of the shift factors α_T is shown on Figure S2. It should be stressed here that, due to the existence of two glass temperatures and the overall complex structure of the studied grafted networks, the tTs should be used with care. Nevertheless, the results shown in Figure 2 appear typical for soft cross-linked gels. Both the segmental relaxation at high frequencies and the polyBA side chain relaxation in the intermediate frequency range can be well distinguished.

At low frequencies the materials do not exhibit a global flow, but instead shows an extended plateau in G' that confirms their elastomeric behavior. The values of G' in this rubbery plateau range are around 3.5 kPa, that is, several orders of magnitude lower than what is typically observed for common polymer rubbers. This finding confirms the supersoft elastomer behavior of the newly developed materials. Interestingly, the BA content that is 33% for H1-BA1 and 85% for H1-BA2, has only a minor influence on the rubbery plateau value of G'. This is most likely related to the relatively low density of the grafted side chains, which we estimated to be in the order of 0.06 and 0.16 polyBA chains per HEA monomeric unit for H1-BA1 and H1-BA2, respectively. Apparently even the relatively small amount of short side chains in H1-BA1 ($M_n \approx 2200$) is enough to swell well the polyHEA based network and ensure supersoft elastomer properties. A further increase of the grafting density even at moderate length of side chains may result in even softer materials.

In conclusion, uniformly cross-linked poly(hydroxyethyl acrylate) based gel networks were produced by cross-linking four-arm star-like poly(trimethylsilyloxyethyl acrylate) polymers prepared by ATRP. Subsequent grafting of short poly(n-butyl acrylate) side chains along the network backbone resulted in the formation of supersoft elastomeric materials with storage shear modulus of less than 5 kPa in the rubbery plateau region, as determined by DMA. This value is orders of magnitude lower than that typically observed for common polymeric rubbers and is caused by the soft nonentangled polyBA side chains, acting as low molecular weight "diluent" and "swelling agent" for the gel network. In contrast to classical diluents, however, these chains are covalently attached to the network and cannot be leached easily. Thus, the newly developed supersoft materials are stable in various environments and may find a number of applications ranging from soft lenses to ionic conductors.

ASSOCIATED CONTENT

Ⓢ Supporting Information
Experimental details and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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