Self-structuring in amphiphilic networks prepared by single conventional radical copolymerization of n-butyl methacrylate and vinylpyrrolidone

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ABSTRACT

Amphiphilic networks segregated in hydrophilic and hydrophobic domains are very attractive materials because they show unique properties related to the combination of both components. In this work, these types of networks have been obtained in a very simple way by single standard bulk radical photocopolymerization of vinylpyrrolidone, and *n*-butylmethacrylate, in the presence of 1 mol % of crosslinkers with different homology towards both components. The crosslinker homology (methacrylate or VP-like functionalities) has shown to have a strong influence on the sol content and on the different properties of the materials, such as segregation or the variation of the storage modulus with temperature and hydration. The experimental results are in good agreement with a theoretical prediction of the network formation carried out assuming that the reaction may be described compositionally by the terminal model. The most efficient crosslinking has been obtained using an asymmetric crosslinker bearing simultaneously methacrylate and VP-like groups.

INTRODUCTION

Standard radical copolymerization of hydrophilic vinylpyrrolidone (VP) and hydrophobic aliphatic methacrylates (generic M) in discontinuous conditions leads to a compositionally heterogeneous collection of chains grouped in two main populations, one rich in VP and a second one rich in M. This collection of chains may actually behave as an amphiphilic system composed of two components, a hydrophilic one, rich in VP and a hydrophobic one, rich in M. This has been shown previously by Gallardo et al¹ who analyzed copolymers obtained from radical copolymerization of VP-and hydroxyethyl methacrylate (HEMA) by electrophoretic analysis (MECK); they observed two well separated peaks, which were assigned to species rich in VP and HEMA respectively. In another example described recently by the same group², it was reported that radical copolymerization of VP and methyl methacrylate (MMA) in methanol renders a self-stabilizing phase separated system, being the disperse and the continuous phases rich in MMA and VP respectively.

In other words, one single and easy radical reaction leads to an amphiphilic system composed of two components, hydrophilic and hydrophobic. The reason of this behavior lies on the well-known differential reactivity of VP and M in radical copolymerization. Assuming that we can use the terminal model to describe the reaction³, and using reactivity ratios from literature^{1,4}, Figure 1 shows the variation of the instantaneous molar fraction of M in the copolymer versus the conversion for equimolar copolymerization in a closed vessel of VP with HEMA or MMA (the two examples mentioned above). The couple tert-butylmethacrylate(tBMA)-VP with a $F_{M0}=0.4$, very close to the reaction studied here, has been included in Figure 1. The copolymerization terminal model⁵ can be used for descriptive purposes although it is well documented that it is only an approximate model⁶.

Figure 1. Theoretical instantaneous molar fraction of M in the copolymer as a function of the conversion for equimolar HEMA-VP (— solid line) and MMA-VP (---dashed line) copolymerizations and for a *t*BMA-VP (...dotted line) copolymerization with $F_{M0}=0.4$. The limiting conversion for the last reaction is indicated as a dotted arrow. The graph has been obtained using the software Copol^{®7} and the reactivity ratios reported in the articles mentioned in the text or in literature. MMA-VP pair, $r_M=4.35$ and $r_{VP}=0.06^4$. HEMA-VP pair, $r_M=7.97$ and $r_{VP}=0.077^1$. *t*BMA-VP pair, $r_M=8.18$ and $r_{VP}=0.032^8$.

Basically, M is much more reactive than VP and it is consumed preferentially. Chains richer in M than feed are formed during the first steps, and when M is being exhausted, chains rich in VP are formed at high conversions^{1,9}. Although the compositional variation is continuous, the graph tends to a step function, which means that there are two main types of species, one that is rich in

M and a second one rich in VP as depicted in the Figure 1. We may call these two collections of chains C_M and C_V , respectively.

This differential reactivity may be explained by the characteristics of VP, which belongs to the group of low activated monomers in radical polymerization. Some authors even include VP in the group of ‘non-homopolymerizable’ monomers¹⁰. According to the classical Q,e scheme of Alfred and Price¹¹ (being Q and e empirical parameters related to the reactivity and polarity, respectively), VP exhibits a Q value of 0.088¹² while *n*BMA exhibits a Q value of 0.82 close to the reference value 1, assigned to styrene. *n*BMA (BMA) is the methacrylate used in this work.

Figure 2. Scheme of the four crosslinker formulations used to prepare the four materials studied in this work: 1-MM; 2-VV; 3-MV, 4-MM+VV.

We propose that this heterogeneity may be useful to prepare amphiphilic networks by copolymerizing BMA and VP in the presence of appropriate crosslinkers. These amphiphilic

networks would incorporate the mentioned C_M and C_V chains, which are comparatively hydrophobic and hydrophilic. Due to the mentioned compositional heterogeneity, an efficient crosslinking of all the chains (i.e. C_M and C_V) is not an easy task, and actually the crosslinker homology may play a key role in the network structure and properties, as it has previously been addressed theoretically by Reinecke et al.¹³ and by Lai¹⁴. Thus, a crosslinker bearing a methacrylate or a VP-like functionality would crosslink preferentially C_M or C_V chains, respectively. Lai prepared HEMA-VP hydrogels using an asymmetric crosslinker bearing methacrylate and vinylcarbonate functionalities (vinylcarbonate is not really VP-like but it shows a similar behavior) and obtained materials with properties that were superior to those of gels prepared with commercial ethylenglycol dimethacrylate (MM of the Figure 2).

In the present work we have prepared BMA/VP networks by bulk radical photopolymerization using the four crosslinking formulations shown in Figure 2 at the crosslinking degree of 1 mol %. The crosslinkers have been named MM, VV and MV as a function of their homology, and a combination of both MM+VV as the 4th formulation. The properties of the networks, such as segregation, mechanical properties or sol content, have been analyzed comparatively.

EXPERIMENTAL SECTION

Reactants

Vinyl pyrrolidone (VP) and *n*-butylmethacrylate (BMA) from Aldrich were distilled under vacuum and stored at 4 °C. The crosslinkers VV and MV were synthesized as described elsewhere^{15,16}. Ethylenglycoldimethacrylate (MM), hexamethyldisiloxane (HMDSO) and 1-hydroxyl cyclohexyl phenyl ketone (HCPK) from Aldrich, as well as the rest of the reactants and solvents, were used as received.

Photopolymerization

Networks were prepared by conventional bulk radical polymerization photoinitiated by UV light. Monomers, crosslinkers and initiator were mixed in the proper amounts. A volume ratio of 1:1 was used for VP:BMA, to balance the contribution of both components. To this liquid bulk monomer mixture, 1 mol % of crosslinker and 0.5 weight % of HCPK were added. Nitrogen was fluxed during 20 minutes to replace the oxygen of the solution. This solution was poured with a syringe in a polypropylene mold with a silicone spacer to attain samples of 0.4 mm. The polymerization was carried out for 40 minutes under UV radiation in a UVP ultraviolet crosslinker lamp (model CL-1000L, 230V). Fresh materials were used in the analysis of the extractable components. The water uptake and dynamic mechanical thermal analysis (DMTA) studies were carried out on materials immersed in water for 48 hours at RT and dried.

Analysis of the extractable components

The extractable components (residual monomer and polymeric sol content) were analyzed by extracting the materials in CDCl_3 and directly performing ^1H -NMR of the supernatant. 5 $\mu\text{L}/\text{ml}$ of - HMDSO - was added as standard to quantify the measurement. A sample of each material (of known weight between 20-40 mg) was immersed and swollen in 1 ml of the solution and kept for 48 hours. The content of the supernatant was analyzed by ^1H -NMR .

The quantification of the three detected extractable species (VP monomer, C_M or C_V sol fractions) has been carried out by comparing the following selected signals to the standard HMDSO at 0.1 ppm; 4.4-4.6 ppm, 2H of VP monomer; 2.9-3.5 ppm, 2H of the VP unit in C_V ; 0.6-1.2 ppm, 6 H of the BMA unit in C_M . The number of mmols has been determined using these equations:

$$mmolsVP = \frac{\frac{A_{4.4-4.6}}{2} 0.42}{A_{0.1}} \quad (1)$$

$$mmolsVP \text{ in } C_V(sol) = \frac{\frac{A_{2.9-3.5}}{2} 0.42}{A_{0.1}} \quad (2)$$

$$mmolsBMA \text{ in } C_M(sol) = \frac{\frac{A_{0.6-1.2}}{6} 0.42}{A_{0.1}} \quad (3)$$

where A is the area given by MestreNova and 0.42 the mmols of HMDSO per ml. All data have been rounded to multiples of 5 due to the technique experimental error.

The compositions of the C_M and C_V sol fractions of the Figure 3 have been estimated comparing the signals mentioned before, according to this equation:

$$f_{BMAcum} = \frac{\frac{A_{0.6-1.2}}{6}}{\frac{A_{0.6-1.2}}{6} + \frac{A_{2.9-3.5}}{2}} \quad (4)$$

Water uptake

The water uptake at equilibrium at RT was determined gravimetrically in three independent measurements. Samples of known weight were immersed in water for 48 hours and weighted.

The water uptake was calculated according to this equation:

$$\text{Water uptake (\%)} = \frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}} 100 \quad (5)$$

Methods

Thermogravimetric analysis (TGA) was performed on a TA-Q500 of TA instruments. Thermograms were obtained under nitrogen atmosphere and using a constant heating rate of 10 °C/min.

^1H NMR analysis was performed in CDCl_3 using a Bruker Avance-300 spectrometer (300 MHz). Chemical shifts are given in the δ scale relative to TMS. Spectra have been analysed using MestreNova software.

Dynamic mechanical thermal analysis (DMTA) was carried out on a Mettler DMA 861e at the appropriate range of temperature and at four frequencies (1, 3, 10 and 30 Hz). Mechanical characterization of the swollen samples was performed on this equipment at the constant temperature of 25 °C. A previous experiment to set the conditions was performed for each sample.

RESULTS AND DISCUSSION

Theoretical description of the reactions and networks

This theoretical description has been carried out assuming that the reaction may be described compositionally by the terminal model; the reactivity ratios of the analogous bulk copolymerization of *tert*-butylmethacrylate and VP⁸ ($r_{\text{M}}=8.18$ and $r_{\text{VP}}=0.032$) will be used for the theoretical description. The equivolumetric feed ratio of BMA/VP used in the work corresponds to an initial feed molar fraction of $F_{\text{BMA}0}=0.4$. The software Copol^{®7} has been used to obtain the theoretical data for this reaction. Figure 1 (dotted line) shows the variation of the instantaneous BMA molar fraction in the copolymer versus the conversion for this equivolumetric copolymerization in a closed vessel. As mentioned in the Introduction, a clear heterogeneity is observed. For the sake of simplicity, the chains have been grouped in only two compositional families named again C_{M} and C_{V} . This classification has been made on a volumetric basis: assuming that the volumes of the units are the same as those of the monomers, the chains with

$f_{\text{BMA}} > 0.4$ or < 0.4 will have a volumetric excess of BMA or VP, respectively, and will belong to C_M or C_V . According to Copol®, this instantaneous limiting composition is formed at a conversion of 0.52, which is therefore the corresponding limiting conversion. The theoretical compositional characteristics, for a reaction at 100% conversion, as well as other relevant data are quoted in Table 1. These data do not take into account the compositional influence in $F_{\text{BMA}0}$ of the crosslinker added at a 1 mol %, which is very low and may be neglected. An example of the calculations is shown in the Supporting Information.

Table 1. Theoretical characteristics of C_M and C_V as determined by Copol® together with some compositional experimental data obtained by $^1\text{H-NMR}$.

	Whole material	C_M , chains rich in BMA 	C_V , chains rich in VP
f_{BMAcum}	0.40	0.73	0.04
Corrected values ^{a)}	0.42		0.05
NMR data ^{b)}		0.72	0.07
w_{BMAcum}	0.44	0.78	0.05
Corrected values ^{a)}			0.06
BMA_{C_M} or BMA_{C_V}		38/40	2/40
VP_{C_M} or VP_{C_V}		14/60	46/60
Corrected values ^{a)}			41/55
Volume ratio C_M/C_V	1.44		
Corrected values ^{a)}	1.60		

f_{BMAcum} and w_{BMAcum} : average BMA molar and weight compositions. BMA_{C_M} , BMA_{C_V} , VP_{C_M} and VP_{C_V} : distribution data obtained by a simple mass balance. The C_M/C_V volume ratio has

been obtained from that mass balance. a) Values corrected for a 95 % of conversion taking into account vitrification, see text. b) Compositions of the sol fraction assigned to C_M and C_V for the systems crosslinked with VV and MM respectively (see text).

A comparative analysis of both families shows that C_V incorporates very few heterologous monomer BMA, while C_M has a 27 mol% of VP. Thus, C_V is very similar to PVP but C_M is a copolymer with a significant incorporation of VP. This asymmetry also explains the C_M/C_V volume ratio that is higher than 1 (despite of the initial volumetric balance of both monomers) due to this significant incorporation of VP to C_M .

Bellow, the theoretical network characteristics are described for the four types of crosslinking systems proposed in the work at 1 mol % of crosslinker. ‘Ideal’ networks will be addressed: reactions at 100 % conversion, infinite molecular weight; effects related to possible segregation, monomer or chain diffusion during the reaction have been also discarded. It has also been assumed that the crosslinker functionalities have the same reactivity than their homologous monomer (BMA or VP). This description will be used as starting point to analyze the ‘real’ networks. In the Appendix, the theoretical development used to obtain the parameters of Table 2 is described.

Table 2. Characteristics of the networks.

Cross. type	Theoretical data					Sol fraction Ext., % ^{a)}		Residual VP ^{b)}		Water uptake (%)
	$\dot{X}_{CM}$	$\dot{X}_{CV}$	p_{CM-CM}	p_{CM-CV^*}	p_{CV-CV}	C_M	C_V	Ext.	TGA ^{c)}	
	27	500	0.902	0.095	0.003	n.d.	95	5	5	72 ± 5

MM										
	112	32	0.054	0.358	0.588	40	n.d.	10	7	90 ± 7
VV										
	44	58	0.222	0.740	0.038	10	n.d.	5	5	74 ± 1
MV										
	44	58	0.478	0.226	0.306	15	n.d.	5	4	79 ± 1
MM+VV										

$\dot{X}_{CM}$ and $\dot{X}_{CV}$ are the average number of units between nodes for the C_M and C_V components respectively; $p_{C_i-C_j}$ is the probability of a link between C_i-C_j , being $i, j = M, V$. * p_{CM-CV} collects the sum of links C_M-C_V and C_V-C_M (see Appendix). CD is the crosslinking degree. Ext. or TGA means that the data have been obtained from the analysis by NMR of the extracts or from the TGA experiments, respectively. n.d.= non detectable. a) % relative to the total C_M or C_V . b) % relative to the total BMA+VP (only VP is detected). c) Weight loss in the interval $130^\circ\text{C} < T < 275^\circ\text{C}$, which has been assigned to VP monomer.

There are clear differences between the four cases of crosslinking. Analyzing $\dot{X}_{CM}$ and $\dot{X}_{CV}$ comparatively, it is clear that the use of MM or VV crosslinks preferentially the homologous component, C_M or C_V respectively. In the case MM is used $\dot{X}_{CV}$ exhibits the higher value of 500. That means that in this case the C_V component is loosely crosslinked. On the other hand, the C_M component forms a densely crosslinked network as indicated by the low value of $\dot{X}_{CM}=27$. The use of VV as crosslinker leads to the opposite case, although the values (mainly the high $\dot{X}$ value

of the heterologous component) are less extreme, $\dot{X}_{CM}=112$ and $\dot{X}_{CV}=32$. This difference, obtaining less extreme values, is related to the fact that C_M incorporates a significant amount of VP while C_V has very few BMA. Thus, p_{CM-CM} in the case of using VV is much higher than p_{CV-CV} in the case of using MM (the latest is almost negligible).

The use of the crosslinker MV or the mixture of crosslinkers MM+VV leads to a more homogeneous crosslinking density (similar values of $\dot{X}_{CM}$ and $\dot{X}_{CV}$). In other words, these two crosslinking systems are more efficient in the crosslinking of this two-component system. Focusing on the probability values, there are however clear differences between these two cases, differences that are related to topological features of the network. While in the case of MV the highest probability is p_{CM-CV^*} (that is the heterolink between C_M and C_V), in the case of MM+VV the highest value corresponds to p_{CM-CM} followed by p_{CV-CV} . In other words, we may say that the use of MV leads to structures with a structural tendency to conetworks, and the use of MM+VV leads to structures with a structural tendency to interpenetrated network, IPN.

In the next section this theoretical prediction is compared to experimental data, and this analysis is used to achieve a deeper understanding of the different crosslinked systems.

Characterization of ‘real’ networks

The extractable species that do not belong to the network structure have been analyzed by NMR. Figure 3 shows representative spectra from the extraction of the systems crosslinked with MM and VV together with homopolymer spectra of PVP and PBMA. All systems exhibited residual VP monomer (as shown in Figure 3 by resolved multiplets centered at 4.2, 3.5, 2.5 and 2.1 ppm, labeled by asterisks). No residual methacrylate was detected in agreement with its

predicted early exhaustion as depicted in Figure 3. In addition to the VP monomer peaks, typical broad polymeric signals corresponding to the polymeric sol fraction (chains not belonging to the network) were detected. As can be seen in Figure 3, when MM is used, the polymeric sol fraction (overlapped with monomer peaks) exhibits a NMR pattern very close to PVP. If VV is used the peaks are similar to those of PBMA. On this basis, and in agreement with the theoretical discussion of the previous section, the sol fraction found when MM is used has been assigned to the C_V component (which is very loosely crosslinked and very rich in VP), while in the case of using VV the sol fraction is assigned to the C_M component (less crosslinked chains). Moreover, the BMA composition of both sol fractions, determined by NMR using the signals **1** and **2** centered at 3.2 and 0.9 (see Experimental Section), have been found to be 0.72 and 0.07, very close to the predicted values of Table 1. This confirms the statement mentioned before theoretically: C_V is close to PVP but C_M incorporates some VP units.

Figure 3: Above: Representative spectra of the extraction study (sol fractions + residual monomer). Below: spectra of homopolymers PVP and PBMA. *=peaks corresponding to residual VP monomer. 1, 2= $-\text{CH}_2\text{-N}$ and $-\text{CH}_3$ signals of VP and BMA, respectively used in the determination of the compositions.

Quantification of the three extractable species (VP monomer, C_M and C_V) has been carried out as described in the section about materials and methods (Table 2). The data have been normalized using the theoretical values of Table 1 (corrected to 95 % conversion).

All reactions showed similar percentage of residual VP monomer, around 5 %. These data of residual VP monomer were in good agreement with the observed TGA weight loss in the interval $130 < T < 275$ °C (see Table 2), which has been assigned to VP monomer. Knowing that the T_g of the linear reference homopolymers are 37 and 170 °C^{12,17} (for PBMA and PVP respectively), we have related this ~95 % conversion to the vitrification of the reaction, that is, to the fact that the T_g of the mixture polymer/monomer exceeds the reaction temperature (room temperature). Both experiments gave a slightly higher value of residual VP for the networks crosslinked with VV. It seems that the vitreous point is reached at slightly lower conversions when the C_V component (that has the higher T_g) is selectively more crosslinked. This non-total conversion in the real system is the first deviation from ‘ideality’ defined in the previous section; correspondingly the characteristics of C_V in Table 1 have been corrected accordingly (see corrected entries). Assuming a fixed conversion of 95 %, the new f_{BMAcum} in C_V is 0.95 and the volume ratio C_M/C_V increases to 1.60.

The quantification of the polymeric sol fraction for the samples is in agreement with the theoretical information of the previous section, which predicted a very loose crosslinking of the C_V chains if MM is used as crosslinker ($\dot{X}_{CV}=500$), a low crosslinking of C_M when VV is used as crosslinker ($\dot{X}_{CM}=112$), and a more efficient crosslinking of both components C_M and C_V when MV or MM+VV are used. The data of Table 2 show indeed that the use of MM produces a network where most of the C_V component (95%) corresponds to the sol fraction, while the use of

VV leads to a 40% of C_M in the sol fraction and very low sol fractions are observed in the other two cases. The low amount of sol fraction in the case of MV or MM+VV crosslinking has surprisingly been proven to be of the C_M type. This may be related to a trapping of the second crosslinker functionality in C_M rich domains formed during the first steps of the reaction, which would make it non accessible and would form a free C_M chain that does not belong to the network. Table 3 summarizes the structural differences for the four crosslinker systems, including some theoretical predictions and some experimental features.

Table 3. Summary of the more noticeable structural features that depend on the crosslinker type.

Crosslinker type	Schematic network topology	Notes
 MM		Almost pure C_M network. Around 95% of C_V belongs to the sol fraction
 VV		Network dominated by C_V chains. 40% of C_M belongs to the sol fraction
 MV		Pseudo-conetwork: high tendency to conetwork topology with majority of C_M - C_V links

MM+VV		Pseudo-IPN: tendency to IPN topology. Majority of C_M-C_M and C_V-C_V links

The networks have been analyzed by DMTA at different frequencies. These measurements have been carried out on the dry forms of the complete polymeric materials (sol + gel) pretreated by immersing them in water for two days followed by drying in order to favor the possible amphiphilic segregation. Extraction experiments of the dried post-treated samples, made with $CDCl_3$ as indicated previously, have confirmed that the residual monomer was extracted during this immersion in water but not the sol fraction, not even the C_V type. It should be noted that the samples swells much more in chloroform than in water.

Figure 4. DTMA analysis of the materials studied in this work.

The variation of the tangent of the phase angle, $\tan(\delta)$, and storage modulus, E' , versus temperature at 3 Hz are depicted for all measurements in Figure 4. The data of $\tan(\delta)$ at 10 Hz have been included to show the change of the $\tan(\delta)$ data as a function of the frequency. In all the cases, the maxima of $\tan(\delta)$ coincide with E' drops.

Networks composed of PVP crosslinked with VV or PBMA crosslinked with MM at 1% have been measured as reference systems. These DMTA analyses can be found under Supporting Information. Assigning the maxima of $\tan(\delta)$ at 3 Hz to the T_g of the systems, it can be shown that the reference monocomponent networks exhibit T_g values of 185 and 67 °C for the PVP and PBMA systems, respectively; being these values slightly higher than those reported for the linear homopolymers, which are 170 and 37°C^{12,17}. This increase can be assigned to the decrease in the chain mobility as a consequence of the crosslinking.

The two-component materials show two clear maxima of $\tan(\delta)$ at temperatures close to the crosslinked reference systems (see Figure 4). Therefore, and in agreement with the previous discussion, these two temperatures have tentatively been assigned to the T_g s of domains rich respectively in C_M and C_V . In other words, the DMTA analysis indicated that there is segregation of these two main components. It is also very interesting that the shape of the curves varies as a function of the crosslinker homology, as will be discussed later.

In order to support the proposed segregation, we have carried out a T_g prediction for the two components C_M and C_V using the Fox equation¹⁸ and using the data obtained in the theoretical prediction (Table 1).

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (6)$$

where w_i is the weight fraction of the given component i (BMA or VP) and Tg_i is the Tg in K of the given homopolymer poly- i (170 and 37 °C for the PVP and PBMA systems, respectively^{12,17}).

These data, together with the experimental maxima of $\tan(\delta)$, have been depicted in Figure 5. If no chain segregation would take place only one maximum would be observed and its temperature would be in between the two reference values. Instead, two maxima are observed and their temperatures are close to the theoretical Tg of C_M and C_V obtained using the Fox equation. This agreement supports the assignments of the two domains as well as the theoretical prediction of the previous section. All experimental evidences suggest that two domains formed by chains rich in BMA and VP, respectively, have been formed, which are compositionally very close to the proposed components C_M and C_V .

Figure 5. Temperatures of the maxima of $\tan(\delta)$ at 3Hz. The dashed lines indicate the values of T_g s predicted according to the Fox equation (see Text).

Some small differences observed in Figure 5 are also in agreement with the previous discussion. Thus, the glass transition temperatures of the component C_M of the systems crosslinked with MM and VV are the highest and the lowest respectively. This is in agreement with the highest and lowest crosslinking degrees of C_M as predicted from the respective $\dot{X}_{CM}$ values of 27 and 112. In a similar way the T_g of the component C_V is slightly higher in the case of a system crosslinked with VV.

A very interesting feature is the influence of the crosslinker type on the shape of the curves of Figure 4. The materials crosslinked with MM or VV exhibit a comparatively low heterologous peak in $\tan(\delta)$. As part or most of the heterologous chains (C_V or C_M respectively) in these two cases belong to the sol fraction, it may be concluded that this sol fraction does not contribute much to the corresponding transition. On the other hand, the use of MV or MM+VV, which gave the lowest sol content and the most efficient crosslinking, leads to two similar peaks in $\tan(\delta)$, that is, to a more balanced contribution of the two types of chains to the transition. This is in agreement with the low sol content and with a formation of domains composed of C_M or C_V chains that belong to the network.

When the best systems crosslinked with MV or MM+VV are analyzed in more detail, a significant feature is observed for the variation of E' with the temperature. In all cases, included the use of MM+VV, the intermediate E' at around 110 °C decreases almost two orders of magnitude but not in the case of the use of MV where E' remains relatively high. Due to the fact that the volume ratio of $C_M/C_V > 1$, we consider the network as dominated by C_M . At 110 °C,

after the first transition, we may imagine the network as a main dominant component above T_g . In the case of MV, however, the lower decrease of the modulus may be related to a higher co-dominance of the two domains as a consequence of the high number of heterolinks C_M-C_V (see Table 2). Again, it seems that MV and its tendency to form a co-network structure leads to a more efficient crosslinking of the two components.

For all relaxations the logarithm of the frequency versus $1/T$ can be fitted using the Arrhenius equation yielding similar Activation Energies in the interval of 300-400 KJ/mol (data not shown). These data confirm the similar nature of the relaxations observed by DMTA.

These amphiphilic networks are able to gain between 70-90 % of water (see Table 2). The networks crosslinked with VV and MM, respectively, showed the highest and lowest swelling degree. This is in agreement with the hydrophilic/ hydrophobic balance of their gel fractions, rich in C_V and C_M , respectively. It is worth remembering that the system crosslinked with VV had 40 % of the C_M chains as sol fraction and the network crosslinked with MM had 95 % of C_V as sol fraction. It is interesting that the use of MV leads to a network with relatively low swelling (lower than the system crosslinked with MM+VV), similar to that of the network with the MM crosslinker. This is again supporting the higher crosslinking efficiency of MV, since in this case the structure with a tendency towards a co-network is more tightly crosslinked. The use of MM+VV, however, shows a tendency to the formation of two interpenetrated networks, each of them more loosely crosslinked. The use of MM or VV exhibits a tendency to form networks where only one of the components participates. As the reaction volume is the same, the MV system gives the tightest network.

Figure 6 shows the storage modulus obtained from DMTA (operating at 3Hz) of the wet and dry samples at 25 °C. At this temperature the dry samples are below the first T_g and they are

rigid materials with a modulus around 2000 MPa. Hydration plasticizes the samples in a manner that strongly depends on the crosslinking type and the water uptake. The samples crosslinked with MM or VV, which showed the lowest and highest water uptake, exhibited obviously the highest and lowest modulus (lowest and highest plasticizing effect). The systems crosslinked with MV and MM+VV showed an intermediate modulus.

Figure 6: Storage modulus at 25 °C of the wet and dry samples obtained by DMTA at 3 Hz. Unpatterned and patterned bars correspond to swollen and dry samples, respectively.

CONCLUSIONS

Amphiphilic networks composed of BMA and VP can be easily obtained by simultaneous radical copolymerization in the presence of a 1 mol% of crosslinker. The materials have shown phase segregation in the dry state in domains rich in BMA and VP, and a water uptake of around 80 %. It has been shown that the homology of the two functionalities of the crosslinker

(methacrylate or VP-like) plays a key role in the crosslinking efficiency (sol content, etc.) and in the properties of the materials in the dry and in the hydrated state (balance of the domains in segregation, storage modulus in the hydrated state, etc.). The ‘best’ crosslinker formulations seem to be MV and MM+VV, which lead to topologies with tendency towards conetworks and IPNs respectively.

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APPENDIX

FE_M and FE_{VP} are the fractions of M or VP functionalities belonging to a crosslinker. $FE_M=0.05$ means that 5 of 100 methacrylate units belong to a crosslinker. These values are given by

$$FE_M = \frac{f_E n_M}{F_{BMAO}} \text{ and } FE_V = \frac{f_E n_V}{(1 - F_{BMAO})} \quad [7]$$

where f_E is the molar fraction of the crosslinker against the total amount of monomers (0.01 in this case); n_M and n_{VP} are the number of M and VP functionalities per crosslinker. $n_M=2$ for MM, 1 for MV, 1 for MM+VV, 0 for VV. $n_{VP}=2$ for VV, 1 for MV, 1 for MM+VV, 0 for MM.

Table 5.

		BMA-VP $F_{BMA0}=0.4$
MM 	FE_M	0.05
	FE_{VP}	0
VV 	FE_M	0
	FE_{VP}	0.033
MV 	FE_M	0.025
	FE_{VP}	0.017
MM+VV 	FE_M	0.025
	FE_{VP}	0.017

Using these data the average number of units between knots for C_M and C_V (named $\bar{X}$) may be calculated as the ratio between total number of units and units belonging to crosslinkers:

$$\bar{X}_{CM} = \frac{1}{f_{BMAcumCM}FE_M + (1 - f_{BMAcumCM})FE_V} \quad [8]$$

$$\bar{X}_{CV} = \frac{1}{(1 - f_{BMAcumCV})FE_V + f_{BMAcumCV}FE_M} \quad [9]$$

The homology of the crosslinking, that is, the type of link C_M - C_M , C_M - C_V (or C_V - C_M) or C_V - C_V (C_i - C_j in a generic way where $i,j=M$ or V) can also be predicted. For a given difunctional crosslinker molecule E_1 - E_2 , where E_k can be any of two functionalities M or VP , the probability for any of the two functionalities of the crosslinker to be incorporate to a generic C_i ($p_{E_k-C_i}$) is

given by the distribution parameters in Table 1, BMA_{CM} , BMA_{CV} , VP_{CM} and VP_{CV} (U_{k-C_i} in a generic way being $U_k=VP$ or BMA):

$$p_{E_k-C_i} = f_{E_1-E_2} U_{k-C_i} \quad [10]$$

being $f_{E_1-E_2}$ the fraction of this type of crosslinker in the total amount of crosslinkers (if there is just one type $f=1$, but when there is a mixture of MM and VV, $f=0.5$).

The probability for a given generic crosslinker E_1-E_2 to link chains C_i-C_j is therefore given by:

$$p_{C_i-C_j} = (f_{E_1-E_2} U_{1-C_i})(f_{E_1-E_2} U_{2-C_j}) \quad [11]$$

Example: BMA-VP crosslinked with MM at 1% molar, $f_{E_1-E_2}=1$ because there is only one type of crosslinker, and the probability for any of the two M functionalities to be incorporated to C_M or C_V is given by the corresponding distribution values of Table 1, $BMA_{CM}=37/40$ and $BMA_{CV}=3/40$. The probabilities of the different links are therefore:

$$p_{CM-CM} = \left(\frac{37}{40}\right)\left(\frac{37}{40}\right) = 0.856 \quad [12]$$

$$p_{CM-CV}^* = 2\left(\frac{37}{40}\right)\left(\frac{3}{40}\right) = 0.139 \quad [13]$$

$$p_{CV-CV} = \left(\frac{3}{40}\right)\left(\frac{3}{40}\right) = 0.006 \quad [14]$$

In this case obviously the majority of the links are C_M-C_M . The * refers to p_{CM} . these calculations $CV^*=p_{CM-CV} + p_{CV-CM}$ and a 2 must be included in the equation. The results of have been quoted in Table 2.

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Author Contributions

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SUPPORTING INFORMATION AVAILABLE:

The SI includes an example of calculation of the data of Table 1 as well as a Figure including the DTMA analysis of the homopolymers PVP and PBMA crosslinked with 1 mol % of MM and VV, respectively. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Radical polymerization