SYNTHESIS OF PROTOTYPE RESINS FOR USE AS BEP INTAGLIO INK VEHICLES CURING BY ELECTRON BEAM RADIATION

Barry J. Bauer
Brian Dickens

U.S. DEPARTMENT OF COMMERCE
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Gaithersburg, MD 20899

Prepared for:
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Bureau of Engraving and Printing
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Annual Report of April 30, 1990
issued December 1990

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Executive Summary

Macromonomers have been studied as components in radiation curable resins. Polymethylmethacrylate macromonomers having methacrylate, acrylate, alkacrylate, and alpha methyl styrene polymerizable end groups and polystyrene having methacrylate end groups were studied.

Thermomechanical analysis of fully cured films of macromonomers and polyethylene glycol diacrylate have one glass transition between the transitions of the individual components, indicating a homogeneous single phase, while equivalent samples made with an unfunctionalized polymer have two transitions, indicating phase separation.

Small angle neutron scattering shows that samples made with macromonomers are much more homogeneous than those made with unfunctionalized polymers. In some combinations, a peak in the scattering curves indicates that microphase separation may occur for high molecular weight macromonomers, while macrophase separation would occur for unfunctionalized polymers. Small angle xray scattering shows that different polymerizable end groups have greatly different uniformities in the fully cured samples.

Curing studies show that the polymerizable end group of the macromonomer can greatly affect the dose required for full cure, with some types inhibiting the cure. High molecular weight and acrylate functionality produce the fastest cure when copolymerized with polyethyleneglycol diacrylate.
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1: Introduction

This work is part of a continuing effort to produce a resin for use in the formulation of inks that will cure by exposure to an electron beam. The resins require a number of different properties in order to be successful such as cure rate, washability, and final physical properties of the cured films. Previous efforts have involved synthesis and characterization of acrylated and methacrylated ionic and nonionic molecules. Two patent applications have been filed in these areas [1-2].

A new approach has been tried this fiscal year in an attempt to produce resins based on combinations of quite different monomers. Instead of synthesizing a variety of related monomers to obtain one with all of the desired properties, existing radiation curable monomers have been combined with new materials, macromonomers, to selectively modify the properties of the monomer blends.

2: Review of Required Resin Properties

2.1: Curing Reaction

A large majority of radiation cured ink resins have polymerizable groups consisting of acrylates or methacrylates. Upon irradiation, free radicals are formed which polymerize the acrylates and form a highly crosslinked network. The optimum dose for the cure is between 1 and 2 megarads (MR). If the required dose is much higher than this range, the paper will begin to degrade during irradiation. Resins that would cure with less of an electron beam dose would probably be too unstable and shelf life would be too short.

All of the work performed at NIST has been on acrylated and methacrylated resins. A variety of synthetic approaches have been used including urethane, phosphazine, siloxane, and ester linkages between the polymerizable components [3-4]. The resins are given water washability through incorporation of ionic or nonionic groups.

Monomers that polymerize through a cationic mechanism are being examined as an alternative to acrylate type of electron beam resins [5]. These polymerizations require a catalyst to produce the ionic species and require more rigorous preparation conditions; impurities such as water need to be excluded. They offer an alternative to acrylate and methacrylate resins, and may have advantages such as lower toxicity [6].

2.2: Water Washability

The intaglio printing process requires that the printing ink be removed from the printing plates with a wiping roller.
This roller needs to be efficiently cleaned before the next pass over the printing plate, or some ink may remain on the nonprinting areas of the printing plate after the wiping. The wiping plate is washed with a liquid to remove the ink. Due to environmental reasons, water is used as the solvent. This requires that the resin be hydrophilic, and that it contains either nonionic water soluble components such as polyethylene glycol (PEG), or ionic groups such as carboxylic acids.

Resins containing acid groups require a basic water solution for washing, typically 1% NaOH and 1% surfactant. Acid groups need to be present above a certain concentration to be effective. The acid group concentration is measured by titration of the resin with alcoholic KOH and is reported as milligrams of KOH required to neutralize the acid groups in one gram of resin. Values of 50 mg KOH/g or greater are usually necessary for proper washing.

Previous work at NIST has examined both ionic and nonionic resins. Acceptable water washability has been demonstrated on a laboratory scale for many of these resins and details of the synthesis have been forwarded to BEP [3-4].

2.3: Resin Viscosity

Intaglio printing inks of interest to BEP require a resin with a viscosity between 50 and 200 poises. Common radiation curable resins are made for other printing processes that require resins with considerably lower viscosities. Therefore there is a general need to produce resins with higher viscosities.

Our previous approach has been to synthesize a monomer that is a larger molecule or has stiffer chains. This increases the resin viscosity to the required value. Another approach is to take a commercially available monomer such as a PEG diacrylate with a viscosity often less than one poise, and to increase its viscosity by incorporation of a low molecular weight polymer. When a polymer is dissolved in a nonviscous liquid, the viscosity can be greatly increased and by controlling the type and amount of the polymer (or macromonomer) any required viscosity can be obtained.

2.4: Cured Resin Physical Properties

One important property of a cured resin is its glass transition temperature (Tg). Cured inks having a Tg significantly lower than use temperature will be rubbery and such films tend to be easily abraded. If the Tg is higher than use temperature, the films may be brittle. A film at Tg has the higher energy dissipation and is therefore the toughest [7].
Another factor that effects physical properties is the morphology of the cured networks. If a network containing more than one type of polymer phase separates into domains of the individual components, the physical properties may be greatly affected. For example, two Tg’s will be present, one for each component. Similarly, the strength and toughness will depend on the morphology formed.

2.5: Toxicity and Sensitization

There are growing concerns over the use of acrylates and methacrylates in ink resins due to the potential toxicity and the possible sensitization caused by them [6]. One possible solution is to replace the polymerizable acrylate functionality with another polymerizable group such as a vinyl ether. There is very little reliable information available on the toxicity and sensitization of other monomer types, however. A program is being planned to use biological methods to screen various monomer types, so that decisions can be made on which types of monomers to study in detail.

Another approach is use monomers that are commercially available which have acceptable toxicity and sensitization characteristics. The properties of these monomers can be modified by addition of macromonomers, to give proper viscosity, washability, cure rate, etc. Since macromonomers are polymeric in nature, it is not likely that they have unacceptable levels of toxicity.

3. Macromonomers

3.1: Introduction

Macromonomers are polymers that are functionalized at one end with a group capable of copolymerizing with conventional monomers. The functional group is typically acrylate, methacrylate, or styrene functionality. Studies of reactivity ratios have shown that the rates of copolymerization of macromonomers are similar to the rates copolymerization of small molecules based on the same functional groups [8]. Therefore, macromonomers can be incorporated into copolymers as efficiently as other monomers.

As discussed earlier, the resins need to have a variety of properties to be successful ink components. These properties can be modified by changing the molecular structure of the electron beam resin, but to obtain these varied structures, a completely new synthesis must be carried out. Also, if slight changes in materials and conditions occur from batch to batch, the final properties will be hard to control.
An alternate method of property control is to make a blend of different resin components each having quite different properties. Properties such as resin viscosity and glass transition temperature of cured films will be intermediate between those of the two pure resins. In this way, properties can be continuously varied between the two extremes. Also quality control can be maintained more easily by blending. For example, if a batch of one component has a variation in viscosity, a slightly different ratio of the other component could regain the desired blend viscosity.

Macromonomers have been studied as components in electron beam resin formulations. Table I lists the macromonomers used in this study. There are three important variables in these macromonomers, the polymeric repeat unit of the macromonomer (polystyrene or polymethylmethacrylate), the polymerizable end group (acrylate, methacrylate, alkacrylate, α-methyl styrene, or unfunctionalized), and the molecular weight (from $M_w = 3400$ to 18400). The molecular weights listed are the ones reported by the manufacturers. The PS macromonomers were obtained from Scientific Polymer Products, and the PMMA macromonomers were obtained from du Pont [9]. Figure 1 gives the chemistry of the repeat units and the end groups.

The comonomers used were styrene and styrene-$d_8$ in the X-ray and neutron scattering studies and a variety of ethoxylated acrylates and methacrylates in the thermal, rheological, and curing studies. Figure 2 shows the molecular structures of the comonomers used.

3.2: Resin Viscosity

There are many resins commercially available for use in radiation cured inks. The intaglio type of printing used by BEP generally requires a higher viscosity than is common in these resins. Polyethylene glycol 400 diacylate has many favorable properties such as cure rate and water solubility, but it has viscosity of about 1 poise, which is much lower than the 50 to 100 poises required by the BEP.

Due to the polymeric nature of macromonomers, mixtures of conventional monomers and macromonomers have viscosities much greater than the comonomers alone. Figure 3 is a plot of $\log(\text{viscosity})$ versus macromonomer concentration for a PMMA macromonomer with an alkacrylate end group and a molecular weight of 7200 g/mole. Viscosities were measured with a Contraves viscometer [9]. At 20°C the viscosities varied by a factor of 375 from pure polyethylene glycol 400 to a mixture with 40 wt. % macromonomer. A 50 wt. % mixture was made, but it had too high a viscosity to be measured at 20°C. At 35°C it had a viscosity of 2300 poise.
By adjusting the macromonomer concentration, the viscosity required for the printing inks can be varied over a very wide range. Other macromonomer variables should also affect the viscosity such as molecular weight and type of repeat unit of the macromonomer. Viscosity seems to be an easily controlled variable by adjusting the type and amount of macromonomer.

3.3: Thermal Properties

Resins of the type examined in the viscosity study were cured using 1 wt. % benzoyl peroxide as a thermal initiator. Samples were cured in aluminum pans sealed in argon filled jars for approximately 24 hours at 60°C.

Thermal properties were measured by Thermo Mechanical Analysis (TMA) with a Perkin Elmer TMS-2 Thermomechanical Analyzer [9]. A sample was cut from the film of approximately 1 mm thickness and 4 mm diameter and placed in the cell between the support and the probe. The sample was cooled to -100°C by placing a cylindrical mantle around it that was cooled by liquid nitrogen. The sample was heated at 10°C/minute up to 150°C, with the sample thickness being continuously monitored.

Figure 4 is a plot of relative sample thickness versus temperature for a fully cured sample containing 10 wt. % macromonomer. The slope of the line is proportional to the thermal expansion coefficient and two linear regions can be seen, one at the low temperature region and one in the high temperature region. These limiting slopes represent thermal expansion coefficients below and above the Tg of the sample. The linear regions are extrapolated and the point of intersection is taken as the Tg as measured by TMA. The points at which the curve first deviates from the straight lines is taken as a measure of the breadth of the transition.

Figure 5 is a plot of the Tg and breadth of transition for samples containing from 0 to 50 wt. % of macromonomer. The glass transitions change continuously from -20 to 70°C over this range. Since the polymerization temperature was 60°C, the 50 wt. % sample may have reached a point of vitrification. The larger the weight fraction of macromonomer included, the broader the transition, but in all cases, only one transition is evident.

It is well documented that compatible blends [10] and copolymers [11] which form a single phase produce materials that have Tg's between those of the individual components. The results shown in figure 5 only demonstrate that no phase separation has occurred between the components. It is possible that any polymer that does not phase separate from the crosslinked matrix would give identical results. In other
words, macromonomers may not be necessary to achieve this control of sample Tg, any unfunctionalized polymer that remains soluble in the network may work.

To test the effect of macromonomers on the thermal properties, two samples were prepared from 35 wt. % PMMA and 65 wt. % PEG 400 diacrylate. The PMMA's were very similar in molecular weight (see Table I). The major difference is that one PMMA was a macromonomer with more than 96 percent alkacrylate functionality at one end while the other PMMA had a hydroxy group at one end which made it incapable of copolymerizing with the PEG 400 diacrylate. The samples were cured as described above and a TMA was taken of each.

Figure 6 is a TMA of the 35 wt. % macromonomer sample which displays a single transition as was described earlier. Figure 7 is the results for a similar sample without the macromonomer functionality. There are quite clearly two thermal events taking place. The lower transition is near that of the Tg of a pure PEG 400 diacrylate network while the upper transition is near that of the PMMA macromonomer itself. This sample seems to strongly be phase separated into domains of nearly pure components.

Depending on the application, a particular morphology may be desirable. A single phase material will have a Tg between the two extremes, and therefore the overall Tg of the cured inks can be easily controlled by proper choice of macromonomer and comonomer. Certain plastic materials can be toughened by having a two phase morphology [7]. In this case an unfunctionalized polymer would be necessary.

3.4 Small Angle Neutron Scattering

Scattering techniques are powerful tools in determining the compatibility of multi-component systems. The phase diagrams of polymer blends have been studied at NIST using small angle neutron scattering (SANS) [12]. Recent work has extended the studies to blends in which some form of crosslinking is present [13-15]. One important class of crosslinked blends are known as interpenetrating polymer networks (IPNs) [16]. One of the many types of IPNs involves dissolving a polymer of one type in a monomer of a second type. The second monomer contains multifunctional units that will form a crosslinked network upon polymerization. It is usually true that the second polymerization is independent of the first, that is, the is no chemical reaction that will lead to crosslinks between the two components.

Small angle scattering can measure the compositional fluctuations in a two component system [17]. It is necessary to label one of the components with deuterium atoms in place of the
hydrogen atoms to provide the necessary contrast for the SANS study. Uniform, homogeneous samples give much lower scattering intensity than ones near phase separation. Once a sample has phase separated, the scattering is very intense and has a different angular dependence. Therefore scattering studies can give morphological information similar to the TMA results.

Seven samples were made for the SANS experiments and their compositions are listed in Table II. All samples were approximately 50 wt. % of one of the two polymeric components. The first polymer is either PS or PMMA. All of the PMMA samples were macromonomers of the alkacrylate type, while the PS samples were both macromonomers of the methacrylate type or unfunctionalized. Both PS types had the same molecular weight and narrow molecular weight distributions. The crosslinked component in each sample was deuterated styrene to provide the necessary contrast for the scattering experiment crosslinked with various amounts of divinylbenzene (DVB), the weight fraction of DVB listed in the table is based only on the second component.

The polymers were dissolved in the styrene-d8/DVB mixture at room temperature along with 1 wt % azobisisobutyronitrile free radical initiator. The homogeneous mixture was poured into a neutron scattering cell used for the scattering experiment and sealed. The cells were placed into a pressure bomb and heated in a 120°C oven for 16 hours. The scattering experiments were carried out at the NIST SANS facility.

Figure 8 is a plot of scattering intensity versus the scattering vector \( q = \frac{4\pi}{\lambda} \sin(\theta/2) \) where \( \lambda \) is the wavelength of the neutron beam and \( \theta \) is the angle of the scattered beam. The top two curves are for the standard semi-II IPNs with 0.5 and 0.3 wt. % DVB respectively. These results are in agreement with the findings previously made for such IPNs [13,15]. If the DVB concentration would be increased to 0.9 wt. % it is expected that these samples would be phase separated.

The lower three curves are for samples made with macromonomers. The very low scattered intensity present indicates that they are much more homogeneous and further from a phase transition than equivalent samples made from unfunctionalized polymers. This indicates that the macromonomer functionality, which allows grafting of the first polymer onto the network formed in the second step, greatly favors the single phase region. The symbol on the axis is the calculated value for zero angle scattering from an equivalent blend, that is, one in which no crosslinking is present. Therefore the semi-II-IPN structure seems to push the polymers towards phase separation, while the grafted IPN structure made from the macromonomers favors the single phase.
Figure 9 gives the results for the PMMA/PSD samples. These scattering curves have a prominent peaks. Previous work on blends crosslinked by exposure to gamma irradiation also gave scattering curves with similar peaks. These peaks were interpreted as being incipient microphase separation [14]. There is no symbol on the axis to show where an equivalent blend would scatter because such a blend would be beyond the point of phase separation.

The scattering results from these model systems demonstrate that there are great differences in the uniformity of samples made with and without macromonomers. These results are consistent with the results of the thermal studies made on PMMA samples with PEG diacrylate networks. If a single phase that gives an intermediate Tg is desirable, then macromonomers must be used.

3.5 Small Angle X-Ray Scattering

Macromonomers can contain a variety of end groups that are capable of copolymerization. The reactivity ratios of such a copolymerization will determine the uniformity of the resulting copolymers [11]. Macromonomers generally have reactivity ratios similar to those of small monomers of the same chemical nature as the macromonomer chain end [8].

Small angle x-ray scattering (SAXS) is similar to SANS in that the range of wavelengths and angles covered are the same. The major differences between the two techniques are the factors that cause contrast to exist between the different components. Contrast in SANS can be conveniently obtained by replacing the hydrogen atoms in one component with deuterium atoms. Contrast in SAXS comes from differences in electron densities which is closely correlated to the mass density of the samples.

PS and PMMA have mass densities of approximately 1.05 and 1.19 g/cc [18-19]. While the contrast factor in SANS is very large compared to the SAXS contrast, there is a large enough density difference for SAXS experiments to give useful results. For much of the time covered by this work, construction at the reactor site has temporarily stopped SANS experiments, so the SAXS technique was developed as a replacement.

Five samples were made with the only significant variable being the type of polymerizable end group on the macromonomer. Table III lists the composition of the SAXS samples. Samples made with alkacrylate and methacrylate groups were optically clear and appeared uniform. The sample made with an acrylate end group was slightly hazy, indicating a very weak phase separation. The α-methyl styrene sample was much more hazy, and the unfunctionalized sample was opaque, indicating ever stronger phase separation.
Figure 10 shows SAXS scattering of the four macromonomer samples. The \( \alpha \)-methyl styrene has the largest amount of low angle scattering and appears the most strongly phase separated of the four. The low angle scattering intensity is in the order \( \alpha \)-methyl styrene > acrylate > methacrylate > alkacrylate. The unfunctionalized PMMA sample was not run since it was obviously the most strongly phase separated.

Figure 11 replots the scattering curves on a logarithmic scattering intensity scale shifted in the y axis for clarity. The \( \alpha \)-methyl styrene sample has a very rapid dropoff in scattering intensity with angle, indicating phase separation. The alkacrylate sample has a peak in the scattering intensity, similar to the peak seen in the SANS data. As with the SANS results, these samples seem to be very uniform.

The four PMMA macromonomers differ only in the polymerizable end group, and low molecular weight analogues are all known to copolymerize with styrene. The morphology of these samples is extremely varied, indicating that slight differences in the polymerization kinetics may produce profound differences in the morphology and hence properties.

3.6 Electron Beam Cure Rates

During the contract period of this work, the electron beam curing apparatus was moved from its location in an ink preparation laboratory to a facility in which it was installed with a research press. This new facility will allow on-line curing of paper printed on a continuous web that closely simulates the type of printing that would be necessary in full scale production of security documents. This will allow scaleup of the testing of electron beam inks, but it meant that no electron beam curing could be tested for the initial 10 months of this project.

Two series of resins were made to test the cure rate of macromonomer/acrylated PEG combinations. The compositions of the resins are given in Table IV. Samples were irradiated at doses between 0.5 and 5.0 MR and the dose to cure is given as the minimum dose required to give loss of film tackiness. The results presented here are for inks formulated from the resins, however the neat resins gave similar dose rates for cure.

The first series studied the effect of the polymerizable group at the end of the macromonomer. Of the five samples tested, the best cure rates came from the acrylate terminated macromonomer and the unfunctionalized PMMA; the tackiness had disappeared with a dose of 1 MR. The methacrylate terminated macromonomer was not available in large enough quantity for formulation into an ink, but cure studies of the neat resin
indicate that about 2 MR would be necessary for full cure. The alpha methyl styrene macromonomer required 2.5 MR and the alkacrylate macromonomer required 3.5 MR. As judged by lack of tackiness, all macromonomers required as much or more dose to give full cure compared to the unfunctionalized PMMA. Certain types of macromonomers seemed to inhibit the curing rate.

If the macromonomer cure rate is lowered by the presence of the end group, then the concentration of end groups should affect the cure rate. The second series of samples varied the molecular weight of the macromonomer, thereby changing the concentration of end groups inversely as the Mn. The three resins had between 10 and 35 weight % macromonomer to produce a resin with a viscosity acceptable for formulation into an ink. This also changed the concentration of end groups. The molar ratio calculated is the ratio of PEG acrylate polymerizable groups to the macromonomer groups. The lowest molar ratio produced an ink that only cured with an unacceptably high dose (5 MR) while the highest ratio produced an ink that required a low cure dose (1 MR).

While the morphology of macromonomer resins cured to a high degree may have advantages over those made with unfunctionalized PMMAs, the dose required may be unacceptably high in some cases. Proper choice of polymerizable group (e.g. acrylate instead of alkacrylate) and macromonomer molecular weight (Mn > 5000) may be necessary to make them a practical resin ingredient.

4. Conclusions

Macromonomers have been used as electron beam ink components and studied by a variety of analytical methods. Rheological studies of PEG diacrylate/PMMA macromonomer samples show that sample viscosity can be varied over a wide range, including the viscosities required for ink formulations. The macromonomers were fully soluble in the comonomers up to 50 weight % macromonomer.

Fully cured samples of these combinations of macromonomers and comonomers were studied by thermal methods. Macromonomer containing samples had glass transitions between those of the pure components, indicating at lease some degree of compatibility. Samples made from unfunctionalized PMMA showed two thermal phase transitions indicating phase separation. The transitions were near those of the pure components indicating strong phase separation.

SANS studies of samples made from macromonomers and crosslinked polystyrene d-8 show that samples made from macromonomers were kept as a single phase while samples made from conventional unfunctionalized polymers would phase
Morphology of samples could therefore be controlled by proper choice of polymers. PMMA/PSD samples made from macromonomers had a peak in the scattering curve indicating that microphase separation may occur in these samples.

SAXS studies of samples made with a variety of macromonomers varying only in the type of polymerizable group show that there is a great variation in sample homogeneity. Slight variations in the copolymerization parameter may therefore result in great variations in sample morphology.

Electron beam cure studies of inks have shown that the macromonomers can inhibit the cure, requiring a larger dose for curing. Acrylate terminated macromonomers give best copolymerization rates with PEG acrylates. The higher the molecular weight, the less the inhibition is seen.

In conclusion, macromonomers give samples with considerably different morphologies and properties than conventional polymers. By controlling the type of macromonomer added to conventional radiation cured monomers, one can obtain viscosity, glass transition, and morphology of interest.
References

1. Patent description of nonionic electron beam resin sent to BEP and processed by the Law Offices of Staas & Halsey.

2. Patent description of carboxylated electron beam resin sent to BEP and processed by the Law Offices of Staas & Halsey.


9. Certain equipment, instrument, or materials are identified in this paper in order to adequately specify the experimental details. Such identification does not imply recommendation by the National Institute of Standards and Technology nor does it imply the materials are necessarily the best available for the purpose.


<table>
<thead>
<tr>
<th>Polymer</th>
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<tr>
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<td>Polymer</td>
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</tr>
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<td>7</td>
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Table III. SAXS samples.

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### Table IV. Doses for cure of inks.

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<th>Functionality</th>
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<th>Wt % MM</th>
<th>Cure Dose (MR)</th>
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<td>-OH</td>
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<td>25</td>
<td>(2)</td>
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<td>25</td>
<td>3.5</td>
</tr>
<tr>
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<td>5</td>
</tr>
<tr>
<td>α-methyl styrene</td>
<td>4,300</td>
<td>25</td>
<td>2.5</td>
</tr>
<tr>
<td>α-methyl styrene</td>
<td>10,200</td>
<td>10</td>
<td>1</td>
</tr>
</tbody>
</table>

Comonomers were PEG acrylates. All inks were formulated at BEP with the exception of the methacrylate macromonomer which was not available in large enough quantities. It was cured as a combination of comonomer and macromonomer.
Figure 1. Chemical structure of macromonomers.

Figure 2. Chemical structure of comonomers.

Figure 3. Log(viscosity) (poises) versus macromonomer concentration for PEG 400 diacrylate and PMMA alkacrylate macromonomer.

Figure 4. Thermomechanical analysis of a fully cured sample of 10 wt. % PMMA alkacrylate macromonomer, 90 wt. % PEG 400 diacrylate. Sample thickness (arbitrary units) versus Temperature (°C).

Figure 5. Glass transition temperature (°C) versus weight fraction macromonomer for fully cured samples of PMMA alkacrylate macromonomer and PEG 400 diacrylate.

Figure 6. Thermomechanical analysis of a fully cured sample of 35 wt. % PMMA alkacrylate macromonomer, 65 wt. % PEG 400 diacrylate. Sample thickness (arbitrary units) versus Temperature (°C).

Figure 7. Thermomechanical analysis of a fully cured sample of 35 wt. % unfunctionalized PMMA, 65 wt. % PEG 400 diacrylate. Sample thickness (arbitrary units) versus Temperature (°C).

Figure 8. Small angle neutron scattering intensity (cm⁻¹) versus scattering vector q (Å⁻¹) for PSH/PSD semi-II IPNs and grafted IPNs.

Figure 9. Small angle neutron scattering intensity (cm⁻¹) versus scattering vector q (Å⁻¹) for PMMA/PSD grafted IPNs.

Figure 10. Small angle xray scattering (arbitrary units) versus scattering vector q (Å⁻¹) for PMMA/PSH grafted IPNs.

Figure 11. Log(small angle xray scattering) versus scattering vector q (Å⁻¹) for PMMA/PSH grafted IPNs.
Polystyrene

\[
R(CH_2CH)_nCH_2CH_2OC=CH=CH_2
\]

Methacrylate

\[
R(CH_2CH)_nH
\]

Polystyrene

Unfunctionalized

Polymethylmethacrylate

\[
R(CH_2C)_nCH_2CH_2CHCH_2OCCH=CH_2
\]

Alkacrylate

\[
R(CH_2C)_nCH_2CH_2CHCH_2COOCH_3
\]

Acrylate

\[
R(CH_2C)_nCH_2CH_2CHCH_2COOCH_3
\]

Polymethylmethacrylate

\[
R(CH_2C)_nCH_2CH_2OCCL_2CHCH_2OCCH=CH_2
\]

Methacrylate

\[
R(CH_2C)_nCH_2CH_2OCCL_2CHCH_2OCCH=CH_2
\]

Polymethylmethacrylate

\[
R(CH_2C)_nCH_2CH_2OCCL_2CHCH_2OCNH\frac{CH_3}{CH_3}
\]

Alpha Methyl Styrene

\[
R(CH_2C)_nCH_2CH_2OCCL_2CHCH_2OCNH\frac{CH_3}{CH_3}
\]

OH (Unfunctionalized)

\[
R(CH_2C)_nCH_2CH_2OCCL_2CHCH_2OC\frac{CH_3}{CH_3}
\]

Figure 1. Chemical structure of macromonomers.
Figure 2. Chemical structure of comonomers.
Viscosities of PEG 400 Diacrylate – Macromonomer Blends at 20 °C

Weight Fraction Macromonomer

Viscosity (Poises)

Figure 3
137-1 A MACROMONOMER 35% 1

DIMENSIONS: 0.012 mm
LOAD: 0.000 g
SCAN RATE: 10.00 deg/min

Figure 6
Figure 10

- $\alpha$-Me Styrene
- Acrylate
- Methacrylate
- Alkacrylate

![Graph showing relative intensity vs. q (Å⁻¹)]
SAXS of Grafted IPNs

α-Me Styrene
Acrylate
Methacrylate
Alkacrylate

Figure 11

\[ \log(\text{Intensity}) + K \]
Macromonomers have been investigated as components in electron beam curing resins for use in intaglio inks. Thermal studies of cured samples of macromonomer-conventional monomer networks show a single transition for macromonomer containing samples and multiple transitions for equivalent samples made with unfunctionalized polymer. Small angle neutron and x-ray scattering studies show that samples made with macromonomers are much more uniform than those made with unfunctionalized polymers. Cure studies show that macromonomers with different polymerizable end groups have very different rates of cure, most of the groups inhibiting the cure.