**Color:**

The absorptions observed for cyclohexanone end at about 325 nm, which is before any absorption of visible light begins, and so only UV light is being absorbed and all of the components of white light are transmitted, which we perceive as meaning a colorless compound.

In cyclohexanethione, however, there is a low intensity absorption maximum at 490 nm, which means that some higher energy (blue-violet) light is being absorbed, and white light minus this component gives the transmission of a pale yellow color.

**Explanation:**

C=S \pi \text{ bonds are weaker than } C=O \pi \text{ bonds (poorer bonding due to the atom size difference between S and O), and so the } \pi\text{-to-} \pi^* \text{ gap for a C=S } \pi \text{ bond is smaller than that of a C=O } \pi \text{ bond.}

The larger \pi\text{-to-} \pi^* \text{ gap for a C=O } \pi \text{ bond means a higher energy (lower wavelength) absorption (187 nm) than its lower energy (higher wavelength) counterpart in the C=S compound (260 nm). Neither of these are absorbing in the visible region. Both have a longer wavelength absorption of lower intensity that would be assigned to n-to-} \pi^* \text{ gaps, which are intrinsically lower in energy than the } \pi\text{-to-} \pi^* \text{ gaps. The n-to-} \pi^* \text{ absorption for cyclohexanone has a maximum at 273 nm, still well away from the visible region, while the n-to-} \pi^* \text{ absorption for cyclohexanethiol has the 490 nm maximum, in the visible region as described above.}
In compound A, the N nbe pair is $sp^2$ and delocalized with the pi system of the benzene ring, and represents extended conjugation relative to compound B, in which the N nbe pair is $sp^3$ and isolated from the pi system.

The analysis is that compound A will have the wavelength of maximum absorption for its pi system (more conjugated) and could show evidence for the even longer wavelength and low intensity $n$-to-$\pi^*$ absorption due to the integration of the N nbe into the pi system.

The conclusion is that compound A will show the $\lambda_{\text{max}}$ 275 & 310 nm, and compound B will have the $\lambda_{\text{max}}$ 260 nm and look more like an isolated benzene ring.
The three possible C₉H₁₀ elimination products are as shown. In the first one drawn here, the new pi bond is conjugated and (E), the second one is conjugated and (Z), and in the third one, the new pi bond is isolated. The third one should have the shorted wavelength of maximum absorption and look more or less like benzene. The other two products should have longer wavelength absorptions because of the extended conjugation. Based upon the description in the question, the conjugation in the (Z) isomer is a little less effective than in the (E) isomer, so its wavelength of maximum absorption would be slightly lower.

The conclusion: the first compound, conjugated (E), is compound Y (slightly longer maxima); the second, conjugated (Z), is compound X (slightly shorter maxima); and the third one, pi-isolated, is compound W (shorted maxima and benzene character in the fine lines).
reported range of absorption values

Yes, these data are consistent. Viewing the range of the reported major absorptions, and using benzene as the baseline: the toluene absorptions are less sharp, have slightly higher $\varepsilon$ values, and show longer wavelengths for the maxima. The relative effectiveness of hyperconjugation on delocalization is anticipated to be low relative to something such as an O nbe pair, and this shows in the higher $\varepsilon$ values and even longer absorption wavelengths for methoxybenzene.
The observation that tetraphenylcyclopentadienone is highly colored is not surprising. It appears to be extensively conjugated and include a carbonyl group with its nbe pairs. Transmitting light in the higher energy blue-violet means that there are significant absorptions at the lower energy end (red-yellow) end of the visible spectrum, which would be consistent with closely packed, low energy transitions in this highly conjugated compound.

The observation that hexaphenylbenzene is colorless is a little surprising. It appears to be extensively conjugated.

One first conclusion might be that the molecule has become so conjugated that all of its absorption region has shifted outside the low energy end of the visible spectrum and into the infrared region.

This is hard to imagine for a couple of reasons. First, even a trailing edge of absorption in the visible region would give this a color (perhaps even more intense than the tetraphenylcyclopentadienone. Second, the infrared region is where you see vibrations, not electronic transition (i.e., the IR spectrum).

The key spectroscopic observation, however, is only available from the UV-vis data: the spectrum for hexaphenylbenzene looks like isolated benzene. And the way to interpret this is that the steric crowding of the six rings around the central one causes them all to rotate out of conjugation and that they are, in fact, seven isolated benzene rings.
(a) (i) 3330 cm\(^{-1}\)  
   the N-H bond

   (ii) 1669 cm\(^{-1}\)  
   the C=O bond

(b) The most significant change: appearance of the OH of an acid, a large and broad absorption ranging from ~ 3500-2500 cm\(^{-1}\). In addition, the position of the C=O will likely shift by about -20 to -30 cm\(^{-1}\) for an acid relative to an ester.

(c) The most significant changes will be the loss of the two absorptions associated with the acid (as described in part (b)): the large and broad absorption ranging from ~ 3500-2500 cm\(^{-1}\) will be gone, and C=O, ~1650 cm\(^{-1}\) will be gone.

(d) The NH bond at 3330 cm\(^{-1}\) will disappear and a new C=O will appear. The C=O is delocalized with both the N and O nbe, and so a relatively lower frequency ~1700-1680 cm\(^{-1}\) might be anticipated.
The vibrational frequency depends on the difference in mass as well as bond order.

A C-H bond and a C-D bond have the same bond order, so no difference based on that.

On the other hand, difference in mass plays a role: the larger the difference, the greater the vibrational frequency (the common trends of NH > OH > CH and C=O > C=C, for instance). There is more difference in mass in a C-H bond than in a C-D bond, and so the vibrational frequency for C-D bonds is anticipated to be lower than C-H.

Which they are.

**Added information:**

And because D is proportionately much heavier than H (double the mass), the effect on the vibrational frequency is pronounced.

The sp³-CD stretches in hexadeuteroacetone have a maximum peak at 2256 cm⁻¹, the sp²-CD stretches for hexadeuterobenzene are at 2389 cm⁻¹, and the sp-CD for dideuteroethyne are at 2700 cm⁻¹.
The two absorptions derive from the higher frequency and sharper OH stretch from OH groups that are not hydrogen bonded and the lower frequency and broader OH stretch for OH groups that are hydrogen bonded.

In polymer A, the equilibrium favors the side of OH groups that are hydrogen bonded, while in polymer B, the equilibrium is more in the other direction.

If the distribution of the OHs and their probability for hydrogen bonding is the same in both polymers (i.e., there are not simply more of these groups closer to one another in polymer A, then the explanation might be that the steric hindrance created by the tertiary alcohols in polymer B does not allow the same degree of hydrogen bonding as in polymer A. Perhaps, for instance, the added bulk of the phenyl rings in polymer B simply creates conformations along the chain where the OH groups cannot get close enough to hydrogen bond, on average, compared with those in polymer A.
all have C=O

<table>
<thead>
<tr>
<th>Structure</th>
<th>C=O Frequency</th>
<th>Other Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(\equiv)CHOH</td>
<td>strong sp CH 3300</td>
<td>broad acid OH 2500+ strong sp-sp CC</td>
</tr>
<tr>
<td>H(_3)C(\equiv)C(\equiv)O</td>
<td>no strong sp CH 3300</td>
<td>broad acid OH 2500+ weak sp-sp CC</td>
</tr>
<tr>
<td>H(_3)C(\equiv)OC(\equiv)H</td>
<td>no strong sp CH 3300</td>
<td>no broad acid OH strong aldehyde CH 2700 strong sp-sp CC</td>
</tr>
<tr>
<td>H(\equiv)CO(\equiv)OCH(_3)</td>
<td>strong sp CH 3300</td>
<td>no broad acid OH strong sp-sp CC</td>
</tr>
<tr>
<td>H(\equiv)OOCH(_3)</td>
<td>strong sp CH 3300</td>
<td>no broad acid OH strong sp-sp CC</td>
</tr>
<tr>
<td>H(\equiv)CO(\equiv)CH(_2)OH</td>
<td>strong sp CH 3300</td>
<td>broad acid OH 3000+ strong sp-sp CC</td>
</tr>
</tbody>
</table>

If you had both of these spectra to look at, you might have a chance to distinguish them, but even then it might be ambiguous; so the greatest confidence is to say it narrows to one of these two:

*If you had both spectra, the C=O frequency of the first one is likely to be lower than the second, as two resonance donors are attached to it:

\[
\begin{align*}
H\equiv\text{C}=\text{O} & \quad \leftrightarrow \quad H\equiv\text{C}=\text{O}^+\text{CH}_3 \\
\end{align*}
\]

whereas the oxygen in the chain of the second one is cross-conjugated and the C=O does not have as much single bond character and would be a higher frequency:

\[
\begin{align*}
H\equiv\text{O} & \quad \leftrightarrow \quad H\equiv\text{O}^+\text{CH}_3
\end{align*}
\]
(a) C=O and CH (aldehyde)  
C=C  
\[\text{compound B}\]

(b) OH (alcohol)  
no C=O  
no C=C  
\[\text{compound H}\]

(c) C=O and OH (acid)  
C=C  
\[\text{compound C}\]

(d) C=O  
no CH aldehyde  
no OH  
no C=C  
\[\text{compound E}\]
The frequency of the C=O stretch is higher more double bond character and lower when there is significant single bond character. The delocalization of the conjugated carbonyl groups means there are added significant resonance contributors with single bond character that do not exist in the saturated compounds, which corresponds to a lower vibrational frequency in the conjugated compounds.
there are many alternative correct structures; compare your answers with other students

(a) C=O and CH (aldehyde)
(b) C=O and no aldehyde CH
(c) OH no apparent sp\(^2\) CH or C=C